Hydrothermal Preparation of Homogeneous Cobalt Oxide Nanomaterials as Stable Anodes for Superior Lithium Ion Batteries

Junke Ou¹ · Shugen Wu² · Hao Wang³

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Abstract

In this study, uniform Co_3O_4 nanoparticles are prepared via a simple and facile hydrothermal synthesis without calcination treatment. When the Co_3O_4 nanomaterials are investigated as anodes for lithium ion batteries, a good electrochemical property is achieved. Particularly, the reversible capacity of the as-synthesized Co_3O_4 nanoparticle has a significant growth from 383 mAh g^{-1} of the initial cycle to 471 mAh g^{-1} of the 300th cycle at 2 A g^{-1} . Moreover, when it recovers to 50 mA g^{-1} after different current densities, a superior reversible capacity of 695 mAh g^{-1} can be reached. Such favorable electrochemical properties will make the as-obtained Co_3O_4 have a good application prospect as anode material for lithium ion batteries.

Keywords Co_3O_4 · Hydrothermal synthesis · Anode · Lithium ion batteries

1 Introduction

Nowadays, rechargeable Li-ion batteries (LIBs) have been universally applied in many portable electronic equipment pieces and have attracted wide attentions to energy storage systems in electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to the advantages of large energy density and excellent cycling property [1–4]. Unfortunately, the commercial graphite as anode shows a small theoretical capacity (372 mAh g^{-1}), greatly restricting its further popularization in the high-power and high-energy devices. In order to meet the increasing requirements of LIBs, researchers have been working on seeking for the replaceable and

available anode materials with superior electrochemical performance [5, 6].

Among various promising anode materials, cobalt oxide (Co_3O_4), a member of transition metal oxides (TMOs), has received extensive concerns in view of its large theoretical capacity of about 890 mAh g^{-1} (2.4 times of commercial graphite anode) and stable chemical properties [7–9]. Unluckily, Co_3O_4 materials are still confronted with some tough drawbacks including low cycling stability and poor rate performance, which are believed to be derived from inferior electronic conductivity and severe volume changes relevant to lithiation/delithiation processes [10, 11]. These defects significantly hinder its practical applications in LIBs. Aimed at handling the above-mentioned problems, the construction of protective layer with carbonaceous component is accounted as an appealing approach, which can improve the electrochemical properties of anode materials [12–14]. Nevertheless, the presence of carbonaceous materials can not only suppress the capacity of Co_3O_4 but also make the preparation process complex [15]. Hence, it is highly desirable to design Co_3O_4 with suitable architectures to obtain high capacity and long-term cycling performance. At present, nanostructured Co_3O_4 has been adopted as anode materials for LIBs, such as nanosheets [16], nanowires [17], nanoplates [18], and nanocubes [19]. For instance, Gou et al. synthesized Co_3O_4 plates and even at 1.6 A g^{-1} , exhibiting the discharge capacity of 217.8 mAh g^{-1} [20]. Co_3O_4 nanosheets showed excellent rate property with the charge

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✉ Junke Ou
ojk0001@163.com

¹ Institute for Advanced Study, Chengdu University, Chengdu 610106, China

² Zhanglan Honors College, Chengdu University, Chengdu 610106, China

³ School of Mechanical Engineering, Chengdu University, Chengdu 610106, China

capacity of 287 mAh g⁻¹ at 1 A g⁻¹ [21]. It is also striking to note that the strategies for the preparation of advanced Co₃O₄ nanomaterials are usually complex and costly. Therefore, it is still a challenge to explore a facile fabrication for the pure Co₃O₄ anode materials with high properties.

Herein, in this study, we have successfully fabricated unique Co₃O₄ nanoparticles with uniform size through a simple and facile hydrothermal method without undergoing any calcination. Typically, the as-prepared Co₃O₄ nanoparticles possess good structural stability and favorable charge transfer reaction for Li⁺ intercalation and deintercalation, which makes obtained Co₃O₄ material show stable electrochemical performances. In particular, after 300th cycle, the reversible capacity of the as-obtained Co₃O₄ gradually increases up to 471 mAh g⁻¹ at 2 A g⁻¹. Compared to the other studies for Co₃O₄, the advantages of this work can be mainly expressed as follows: (1) The preparation method for Co₃O₄ is simple and facile, without involving any carbon coating and pyrolysis process; (2) the uniform-sized Co₃O₄ nanoparticles accelerate Li-ion and electron transfer, which contributes to achieving high rate performance; and (3) the electrochemical performance of the as-obtained Co₃O₄ is superior and can be improved with the increase in cycles (383–471 mAh g⁻¹ from the first cycle to the 300 cycles at 2 A g⁻¹).

According to the previous literature on developing nanomaterials as anodes for LIBs, Co₃O₄ nanoparticles still show some obvious properties. For one thing, many nanomaterials as anodes usually need the hybridization of a variety of materials or addition of coated carbon followed by calcination [22, 23]. For another, TiO₂@SnO₂ nanofibers delivered a specific capacity of 378 mAh g⁻¹ at a current density of 2 A g⁻¹ [24], while in our study, a high capacity of 471 mAh g⁻¹ could be obtained by Co₃O₄ nanoparticles at 2 A g⁻¹. Meanwhile, Zan et al. reported that SnO₂/Fe₂O₃ hybrid nanofibers demonstrated an outstanding cycling stability in contrast with pure SnO₂ [23], so we can also add another transition metal oxide into Co₃O₄ to further

improve the performance in the future study. To sum up, the as-obtained Co₃O₄ nanoparticles are expected to make a great improvement in the development of nanomaterials for LIBs and realize large-scale production.

2 Experimental

2.1 Synthesis of Co₃O₄ Material

As described in Scheme 1, 80 mg cobalt acetate was ultrasonically dissolved in the solution (1 ml distilled water and 20 ml ethanol) and 1 ml ammonia (NH₃·H₂O) was put into the above solution drop by drop. Afterward, the above solution was needed to be stirred magnetically for 0.5 h to gain a uniform solution. The solution was placed in an autoclave reaction kettle and increased to 80 °C for 8 h. Subsequently, the reaction temperature went up to 150 °C for 3 h. After being cooled down, the obtained dark solutions were centrifuged, washed with water and ethanol for three times, and dried in vacuum at 60 °C overnight.

2.2 Electrochemical Testing

The electrochemical measurements of the Co₃O₄ were conducted in CR2032 coin-type batteries. For preparing working electrodes, a mixture of 80 wt% active material, 10 wt% polyvinylidene fluoride (PVDF), and 10 wt% acetylene black in N-methyl-2-pyrrolidone (NMP) was uniformly pasted onto a pure Cu foil and then dried at 80 °C in vacuum. Afterward, all coin batteries were fabricated in an Ar-filled glove box using the as-synthesized Co₃O₄ as the active electrodes (the mass loading was determined to be 1.0 mg cm⁻²), Li foil as a counter-electrode, and Celgard-2400 as the separator. The electrolyte was 1 M LiPF₆ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 by volume) with 2% VC. Electrochemical

Scheme 1 Illustration of synthesis process for Co₃O₄ nanoparticles

tests were performed on the NEWARE battery tester ranging from 0.01 V to 3.0 V, and cyclic voltammetry investigations are performed at a scan rate of 0.1 mV s^{-1} .

2.3 Materials Characterizations

The XRD measurement was investigated at a scan rate of 2° min^{-1} by a TD-3500 powder X-ray diffractometer (Tongda, China) with $\text{Cu-K}\alpha$ radiation. The morphology and crystal structure of the materials were studied applying a Hitachi S-4800 scanning electronic microscope (SEM) and a FEI Tecnai G2 20 transmission electron microscope (TEM) (Hillsboro, OR, USA). The X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos XSAM 800 spectrometer (Manchester, UK).

3 Results and Discussion

The X-ray powder diffraction (XRD) pattern of the as-obtained Co_3O_4 is depicted in Fig. 1a. All the diffraction peaks can be corresponding to the cubic phase of Co_3O_4 [25]. Meanwhile, no additional peaks can be seen in the XRD pattern, revealing the high purity of the material. SEM was used to observe the morphology of a typical Co_3O_4 sample. Figure 1b shows that large amount of Co_3O_4 nanoparticles agglomerate to some extent. The more detailed information about the chemical composition and elemental valence state of the Co_3O_4 nanoparticles was investigated by X-ray photoelectron spectroscopy (XPS). In Co 2p spectrum (Fig. 1c), there are two strong peaks with the binding energy at 795.4 eV and 780.3 eV, which are ascribed to the Co 2 $p_{1/2}$ and Co 2 $p_{3/2}$ spin-orbit peak of Co_3O_4 , respectively [26]. The binding energy difference between the peaks of Co 2 $p_{1/2}$ and Co 2 $p_{3/2}$ is almost 15 eV, suggesting the presence of

Fig. 1 XRD pattern of Co_3O_4 **a**, SEM image of Co_3O_4 **b**, Co 2p **c** and O 1s **d** spectra of Co_3O_4

Co^{2+} and Co^{3+} species in the sample [27]. The peaks at about 803 eV and 787 eV are associated with the $\text{Co } 2p_{1/2}$ and $\text{Co } 2p_{3/2}$ shake-up satellite of Co_3O_4 , respectively [28]. Additionally, the peak located at about 707 eV is described as the Auger peak of cobalt [29]. The $\text{O } 1s$ displayed in Fig. 1d can be fitted into three major parts. The peaks at about 532.0 eV and 533.6 eV are associated with oxygen vacancy and absorbed oxygen, respectively, and the peaks centered at 529.6 eV and 530.9 eV are both due to lattice oxygen [30, 31]. Besides, the peak with a higher binding energy of 531.6 eV may be attributed to the hydroxyl groups (OH) [32].

Figure 2a depicts a low-magnification TEM image of Co_3O_4 , from which it can be seen that Co_3O_4 nanoparticles are uniformly distributed without any obvious aggregation. The high-resolution TEM (HRTEM) image of Co_3O_4 displayed in Fig. 2b clearly further shows the homogeneously Co_3O_4 nanoparticles with small particle sizes of approximately 4–9 nm, which is consistent with Fig. S1. Additionally, Co_3O_4 possesses two interplanar spacings of 0.23 and 0.46 nm, which is in accordance with specific

lattice planes (311) and (111) of Co_3O_4 crystal, respectively [33]. The STEM element mapping analysis (Fig. 2c) further discloses the coexistence and evenly distribution of cobalt and oxygen elements for Co_3O_4 .

The cyclic voltammetry (CV) profiles of Co_3O_4 electrode for the initial three cycles at a scan rate of 0.1 mV s^{-1} ranging from 0.01 to 3.0 V are exhibited in Fig. 3a. In the first cycle, a strong cathodic peak appears at 0.8 V, which is ascribed to the reduction of cobalt ions to Co metal, the generation of amorphous Li_2O , and the generation of solid–electrolyte interface (SEI) film [34, 35]. Another inconspicuous cathodic peak was centered at 1.7 V (disappeared in the subsequent cycles), which may be because a small number of lithium ions enter the crystal structure of Co_3O_4 [36]. Besides, there are two tiny peaks located at 1.4 and 2.0 V in first anodic scan, which pertains to CoO_x ($0 < x < 1$) and the oxidation process of Co to Co_3O_4 , respectively [37, 38]. The intensities of the cathodic peaks are significantly weakened in the other cycles because the SEI film is formed between the

Fig. 2 TEM images **a**, **b** and STEM element mapping images **c** of the Co_3O_4 . Inset in **b** showing the HRTEM image of Co_3O_4

Fig. 3 Electrochemical behaviors of Co₃O₄ anode materials, CV curves of Co₃O₄ materials during the initial three cycles **a**, charge and discharge curves at a current density of 50 mA g⁻¹ **b**, rate property at different current densities **c** and the cycling performances during 300 cycles at 2 A g⁻¹ **d**

electrolyte and nanostructured electrode [9]. Generally, the electrochemical reactions involved can be illustrated as follows [39]:

Figure 3b depicts the charge–discharge profiles of Co₃O₄ with a current density of 50 mA g⁻¹ ranging from 0.01 V to 3 V. It can be clearly observed that a well-defined long potential plateau is at about 1.1 V, which is due to the reduction of the intermediate Li_xCo₃O₄ to metallic Co [40, 41]. The first charge and discharge capacities are 599 and 782 mAh g⁻¹, respectively, accompanied by a Coulombic efficiency (CE) of 76.6%. The first irreversible capacity loss and relatively low CE may arise from the generation of the SEI layer at the electrolyte interface, lithium storage, and electrolyte decomposition [42–44]. In the 2nd, 10th, 20th, and 50th cycles, Co₃O₄ electrode shows reversible capacities

of 556, 635, 656, and 690 mAh g⁻¹, respectively, which indicates that Co₃O₄ is inclined to possess good capacity retention as well as much higher capacity. As demonstrated in Fig. 3c, the rate property of Co₃O₄ is evaluated at different rates ranging from 0.05 A g⁻¹ to 5 A g⁻¹. The average reversible capacities are 753, 681, 614, 475, 462, 337, and 122 mAh g⁻¹ at 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 A g⁻¹, respectively. Impressively, the average reversible capacity of 695 mAh g⁻¹ with the 92.3% of the initial reversible capacity can still be obtained when it is recovered to 0.05 A g⁻¹, which is indicative of a fascinating recovering ability of the electrode. The cycling property of the Co₃O₄ is conducted at 2 A g⁻¹ in Fig. 3d. Generally, after 300th cycle, Co₃O₄ electrode still works pretty stably with a reversible capacity of 471 mAh g⁻¹ even at a high current density of 2 A g⁻¹. The phenomenon of gradually increasing reversible capacity upon cycling may be caused by the reversible generation of a polymeric gel-like film evolving from kinetic activation during the charge/discharge process [45].

The electrochemical impedance spectroscopy (EIS) investigations were conducted at different cycles (10th, 30th, and 50th at 50 mA g^{-1}) in the frequency in the range of 100 kHz and 10 MHz for the sake of illuminating charge transfer and Li^+ diffusion kinetics. As illustrated in Fig. 4, all the Nyquist plots present similar shape feature of two depressed semicircles in the high-/medium-frequency regions followed by a low-frequency linear tail. The first semicircle in the high frequency is associated with SEI resistance (R_{SEI}), the second semicircle across the medium-frequency region denotes charge transfer impedance (R_{ct}) in the interface between the electrode and electrolyte, while the low-frequency linear tail is regarded as the Warburg impedance (Q_{w}) revealing the solid-state Li^+ diffusion process within bulk electrodes [8, 46, 47]. In general, the intercept of the first semicircle at the real axis (Z') suggests the electrolyte resistance (R_s) [17, 48]. Based on

the equivalent circuit, the fitted physical parameters are summarized in Table 1. Furthermore, the SEI capacitance and interfacial capacitance can be defined as Q_{SEI} and Q_{d} , respectively [49]. It is worth mentioning that the Co_3O_4 takes possession of the lowest charge transfer impedance (11.14Ω) after 50 cycles, accounting for the improved charge transfer activity at the interface between the Co_3O_4 nanoparticles and the electrolyte with the increase in the cycle times. These results can be confirmed with the results of the cycling performances in Fig. 3b and d. Notably, a maximum slope can be observed at the 50th cycle, which may correspond to the lowest Q_{w} [50, 51]. As a consequence, the Co_3O_4 materials synthesized are able to effectively enhance the Li-ion and charge diffusion during the repetitive Li-ion insertion/extraction process.

Table 1 Kinetic parameters derived from the Nyquist plots of the Co_3O_4 after different cycles

Cycles	$R_s (\Omega^{-1})$	$R_{\text{SEI}} (\Omega^{-1})$	$R_{\text{ct}} (\Omega^{-1})$
10th	4.033	6.804	43.81
30th	5.78	9.827	13.21
50th	5.848	7.589	11.14

4 Conclusion

In this work, a facile and simple hydrothermal strategy for the synthesis of Co_3O_4 nanoparticles is described. Such Co_3O_4 nanoparticles with uniform size provide beneficial transport kinetics for both Li-ions and electrons. As a result, Co_3O_4 electrode provides growing cycling performances (about 471 mAh g^{-1} at 2 A g^{-1} after 300 cycles) and a remarkable capacity retention (92.3% of the initial capacity when it returns to 50 mA g^{-1}). In terms of the facile preparation and stable electrochemical properties as shown, this simple approach to prepare nanoparticles can be further applied in other transition metal oxides and serve as a promising strategy to explore alternative anode materials for applications in new-generation LIBs.

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Fig. 4 EIS of Co_3O_4 electrode at 10th, 30th, and 50th cycles at 50 mA g^{-1} with the equivalent circuit

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