Co$_3$O$_4$/Co nanoparticles enclosed graphitic carbon as anode material for high performance Li-ion batteries

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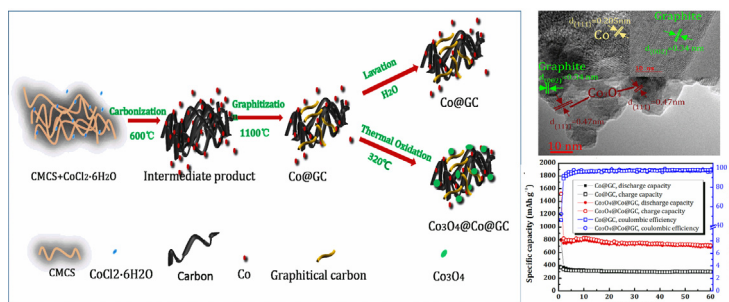
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HIGHLIGHTS

- A composite of Co$_3$O$_4$, Co, graphitized carbon is proposed for LIBs which is seldom reported.
- It is prepared by Co-catalytic-graphitization of carboxymethyl chitosan derived carbon.
- The composite delivers improved electrochemical performance.
- The enhanced performance is due to the conductive Co and graphitic carbon and high-capacity Co$_3$O$_4$.

GRAPHICAL ABSTRACT

ABSTRACT

The composite of Co$_3$O$_4$, Co and graphitized carbon is synthesized by carbonization and cobalt-catalyzed-graphitization of carboxymethyl chitosan, followed by low-temperature thermal oxidation. At the high temperature, the Co(+2) is reduced to metallic Co and the produced Co acts as a catalyst for the graphitization of the pyrolytic carbon. The low-temperature oxidation is conducted to selectively oxidize Co to Co$_3$O$_4$ while the carbon remains unreacted. The structure analysis indicates that three crystal phases (graphite, metallic Co, Co$_3$O$_4$) accompanied with amorphous carbon are co-existed in the composite. Morphological results demonstrate that a lot of graphite grains around the Co element are distributed in the carbon. The electrochemical testing results indicate that the composite shows good electrochemical performance. It delivers a reversible capacity of 843 mAh g^{-1} at low current density, and remains 88.9% after 60 cycles at 200 mA g^{-1}. Even performed at 1 A g^{-1}, it also exhibits 493 mAh g^{-1}. The performance improvement is mainly due to the high capacity of Co$_3$O$_4$, high conductivity of graphitic carbon and metallic cobalt, the porous structure offering enough ion transport pathways and relieving the strain during cycling.

1. Introduction

With the popularity of consumer electronics and renewable energy, Lithium-ion batteries (LIBs) as one of the most efficient energy storage devices, have attracted more and more attentions due to their high specific energy, long cycle life and high safety [1–10]. As one of the components, the anode materials have great

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effects on the performance of the LIBs [11–13]. Graphite is the most widely used anode material for commercial LIBs. However, the low theoretical capacity (372 mAh g^{-1}) inhibits the further application of graphite for next-generation high-energy LIBs [14,15]. Therefore, it is of great significance to develop new anode materials with high capacity, high safety and good cycle stability.

Transition metal oxides, such as cobalt oxides [14,16–19], iron oxides [20–23], nickel oxides [24–26], and multi-metal oxides [27–29], have attracted a lot of attentions because of their high capacity and easy production. Among the various types of TMOs, Co_3O_4 shows the most potential with a high theoretical specific capacity (896 mAh g^{-1}) [30]. However, this material suffers from the poor conductivity and a large amount of volume changes during the process of charging and discharging, which lead to poor rate capability and rapid capacity fading [31,32]. Lots of works have been reported to enhance the cycling stability of Co_3O_4. Among those strategies, nanocrystallization is one of the most important ways to shorten both the electron and Li$^+$ diffusion pathways [33], which can significantly improve the electrochemical performance. Up to now, various Co_3O_4 nanostructures such as nanorod [34], nanotube [35] and nanofiber [36] have been reported as anode materials with enhanced electrochemical performance. Another effective strategy is to composite Co_3O_4 and other stable and high-conductive materials. Among them, carbonous materials are the good choice. Co_3O_4 materials composited with high-conductive carbons have been reported to show improved conductivity, increased surface area and enhanced cycling stability [37,38].

In this work, a composite of Co_3O_4, Co and graphitized carbon is proposed and prepared by carbonization and cobalt-assisted-graphitization of carboxymethyl chitosan, followed by low-temperature thermal oxidation. It has been reported that the metallic cobalt can promote the graphitization of carbonous materials [39–41]. Therefore, we expect the highly graphitic characteristics of the carbon in the prepared composite with the addition of cobalt salt in the carbon precursor since the cobalt salt could be reduced to metallic cobalt during the high-temperature pyrolysis. In addition, after the low-temperature thermal oxidation, the metallic cobalt is able to transfer to Co_3O_4 nanocrystals, which can increase the capacity of the composite. This complex structure is seldom reported before. We expect this composite to show good electrochemical performance as LIBs' anode.

2. Experimental

2.1. Synthesis of materials

$CoCl_2 \cdot 6H_2O$, carboxymethyl chitosan (CMCS) were mixed with a defined amount of deionized water. The $CoCl_2 \cdot 6H_2O$/CMCS ratio was fixed to 9 mmol g^{-1}. After that, the mixture was dried at 110 °C for 2 h to remove the moisture, then heated to 600 °C for 2 h, and finally heated up to 1100 °C for 3 h under Ar atmosphere. The heating rate was 2 °C min^{-1}. Finally, the sample was sintered at 320 °C in the air to selectively oxidize Co metal. The final product was marked as Co_3O_4@Co@GC. The sample before thermal oxidation was named as Co@GC. The graphitic carbon without Co and Co_3O_4 (GC) was prepared by HCl solution leaching of Co@GC sample.

2.2. Materials characterizations

The powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) using Cu Kα radiation was employed to identify the crystal structure of the obtained materials. The morphology and microstructure were observed by scanning electron microscopy (SEM, JEOL, JSM-

5612LV) and transmission electron microscopy (TEM, Tecnai G12, 200 kV). The cobalt and carbon contents were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS intrepid XSP, Thermo Electron Corporation) and C-S analysis equipment (Eltar, Germany), respectively.

2.3. Electrochemical measurements

The work electrode was made by mixing the 80 wt% prepared materials, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride in N-methyl pyrrolidinone until homogeneous slurry was obtained. Then the slurry was coated onto a copper current collector and dried at 120 °C for 6 h in the oven. The coating thickness of electrode was kept at 120 μm by coating machine and the loading density of active materials was controlled to 1.00 ± 0.05 mg cm^{-2}. After that, it was punched to form rounded pieces with a diameter of 12 mm. In order to test the electrochemical performance, the half cells (coin-cell CR2032) with the prepared electrode as working electrode and the lithium metal foil as the counter electrode were assembled in an Ar-filled glove box. A microporous membrane (Celgard 2400, Celgard Company, USA) was used as the separator and 1 mol L^{-1} LiPF$_6$ in EC/EMC/DMC (1:1:1 in volume) solvent was used as the electrolyte. The galvanostatically charge-discharge tests were conducted by a Neware battery analyzer in the voltage range of 0.01–3.00 V vs. Li$^+$/Li. Cyclic voltammetry (CV) test was performed by using CHI600E electrochemical workstation at a scanning rate of 0.1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was tested by a CHI660A electrochemical workstation by applying an AC voltage of 5 mV amplitude in the frequency range of 0.01–10^5 Hz.

3. Results and discussion

The structural information of the prepared Co@GC and Co_3O_4@-Co@GC samples were collected by XRD technique. The results are shown in Fig. 1. In the XRD pattern of Co@GC sample before thermal oxidation, characteristic peaks of metallic cobalt (JCPDS NO. 15-0806) and graphitic carbon (JCPDS NO. 26-1079) are clearly presented, indicating that the Co (+2) is reduced to Co(0) at the reducing atmosphere and a high-order graphitic carbon is formed at high temperature, which are further confirmed by the XRD and Raman results of the GC sample (Fig. S1). The formation of graphitic carbon is attributed to that the metallic Co can act as catalysts to promote the graphitization at ~1000 °C [39,42]. It is
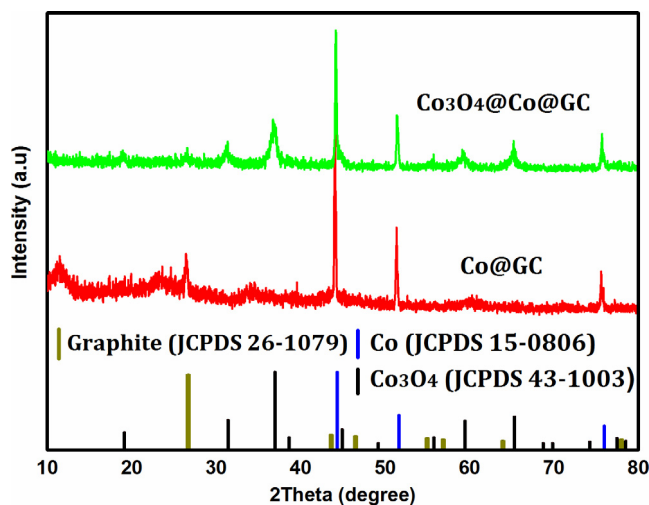

Fig. 1. XRD pattern of the prepared Co_3O_4@Co@GC and Co@GC.