Mesoporous NiCo$_2$O$_4$ nanoparticles as cathode additive for high-performance lithium sulfur battery

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Abstract. Lithium sulfur batteries with high theoretical energy density are promising candidate as next-generation energy storage system. However, practical strategies for releasing the true potential of sulfur cathode are still needed. Therefore, in this work, the NiCo$_2$O$_4$ with hybrid nanostructure is manufactured in a simple atmospheric and water-based method. The surface area of the mesoporous NiCo$_2$O$_4$ is determined to be about 59.99 m$^2$g$^{-1}$. The electrode with NiCo$_2$O$_4$ exhibits a high initial capacity of 1399.8 mAh g$^{-1}$ at the current density of 0.1 C. These results indicate that the electrode material has enormous potential as high-performance cathode materials.

1. Introduction

Rechargeable Lithium-sulfate batteries (Li–S) are one of the most attractive electrochemical storage devices because of their high theoretical capacity of 1675 mA h g$^{-1}$ and high energy density of 2600 Wh kg$^{-1}$ [1,2]. However, due to intrinsic problems such as low electrical conductivity of sulfur, volume change during cycling and shuttle effect of polysulfides, the solution for high-performance Li-S batteries is still an open question [3]. In recent years, ternary transition metal oxides have attracted considerable attention because of their contribution to the oxidation and reduction processes combined for both metal ions [4]. Specifically in Li-S batteries, hollow NiCo$_2$O$_4$ nanofibers was fabricated by electrospinning the fiber precursor followed by calcination. Subsequently, a sulfur-amine chemistry method was applied to load sulfur onto NiCo$_2$O$_4$ nanofibers [5]. In another study, NiCo$_2$O$_4$ nanofibers were prepared by hydrothermal treatment of the precursors followed by annealing [6]. Very recently, metal salts and glycerol were mixed in isopropanol, followed by solvothermal and annealing treatments to obtain the NiCo$_2$O$_4$ Nanoflower [7]. However, these methods involves complicated synthesis, high pressure thermal treatment and/or sulfur loading process. Therefore, it is necessary to develop an easy, low-cost and scalable strategy for applying NiCo$_2$O$_4$ material with desired nanostructure to promote the electrochemical processes in Li-S batteries.

Here in this work, we illustrate a strategy for synthesizing NiCo$_2$O$_4$ nanoparticles via an atmospheric and water-based method without using organic solvent. The as-synthesized NiCo$_2$O$_4$ nanoparticles possess porous nanostructure, which provides abundant active surface for adsorption of soluble sulfur species and channels for ionic transport. As a result, the cathodes with NiCo$_2$O$_4$ nanoparticles exhibit high discharge capacity, good stability and excellent rate capability, suggesting great potential for practical application in high power Li-S batteries.
2. Experimental method:
All of the purchased chemicals with grade analytical and used without any pretreatment were bought from Sigma-Aldrich. For the preparation of the NiCo$_2$O$_4$ nanoparticles with hybrid nanostructure, 0.8 mmol of Ni(NO$_3$)$_2$·6H$_2$O, 1.6 mmol of Co(NO$_3$)$_2$·6H$_2$O, 2.0 mmol of hexamethylenetetramine (HMT) and 0.4 mmol of trisodium citrate dihydrate (TSC) were added into 40 mL of deionized (DI) water, followed by ultrasonic for 30 minutes. The above solution was kept in the oil bath at 90 °C for 6 hours with agitation. After cooling naturally to room temperature, the black precipitate was collected by centrifugation at 8000 rpm for 10 min, and washed with DI water and ethanol for three times, respectively. Lastly, the precipitate was dried for 6 h at 150 °C, and was heated to 500 °C for 3 hours in the air at a heating rate of 1 °C min$^{-1}$ to obtain NiCo$_2$O$_4$ nanoparticles.

X-ray diffraction patterns (XRD) were obtained using the advanced X-Ray Diffractometer of Bruker D8 with Cu Kα radiation ($\lambda = 1.5406$ Å) at a voltage of 40 kV and a current of 40 mA. The N$_2$ adsorption-desorption were determined by BET measurements using a Quanta chrome instrument surface area analyzer. The nanostructures and morphological properties of nanomaterials were characterized by scanning electron microscopy (SEM, FEI 450).

Standard 2025 coin cells were assembled to assess the electrochemical performances. In a glove box filled with very pure Argon, pure lithium was used as reference electrodes with Celgard 2400 membrane as separator. 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 in volume) with 2% LiNO$_3$ as additive was used as the electrolyte. Working electrodes were prepared by casting a mixture containing 20 wt% NiCo$_2$O$_4$ nanoparticles, 60 wt% of sulfur, 10 wt% of conductive carbon (Acetylene black), and 10 wt% of the polymer binder (polyvinylidene flor uoride, PVDF) in N-methylpyrroolidone (NMP) onto the Al foil, followed by drying in vacuum at 60 °C for 12 hours. Cyclic voltammetry (CV) were performed on CHI660c electrochemical workstation (Chenhua, Shanghai). All discharge and charge measurements were performed at room temperature on the LAND CT-2001A system (Wuhan, China).

3. Results and Discussion
Typical SEM images with different magnification are shown in Figure 1. It is worth noting that the entire nanoparticle surface is covered by nanostructures. These porous nanostructures can provide abundant adsorption sites for the interaction between NiCo$_2$O$_4$ and soluble polysulfides. Moreover, these structures are useful in enhancing electrolyte infiltration and ionic transfer.

![Figure 1. SEM images of NiCo$_2$O$_4$ nanoparticles. The scale bars are (a) 1 μm and (b) 300 nm, respectively.](image)

X-ray diffraction (XRD) measurement was performed to examine crystal information of NiCo$_2$O$_4$ product as shown in Figure 2a. The specific diffraction peaks of the spinel NiCo$_2$O$_4$ phase (JCPDS...
card 20-0781) can be well identified. No additional peaks of potential impurities have been observed, suggesting a high purity of NiCo$_2$O$_4$ product. The specific surface area and pore size distribution of the selected sample were investigated by conducting nitrogen (N$_2$) adsorption–desorption isotherm measurements. As shown in Figure 2b, the N$_2$ adsorption–desorption curve of porous NiCo$_2$O$_4$ can be assigned to the IV-H$_2$ type isotherm, indicating the mesoporous nature of the particle structure. According to the Brunauer-Emmett-Teller analysis, the NiCo$_2$O$_4$ nanoparticles possess a very high surface area of 59.99 m$^2$g$^{-1}$. The inset of Figure 2b shows the pore-size distribution plot calculated by the Barrett Joyner-Halenda method of the adsorption branch. The average pore size distribution and volume are 10.66 nm and 0.26 cm$^3$g$^{-1}$, respectively.

![Figure 2](image.png)

**Figure 2.** (a) XRD patterns and (b) N$_2$ adsorption-desorption isotherm and pore size distribution curve (inset) for NiCo$_2$O$_4$ sample.

Figure 3a shows the features of the charge/discharge curves at 0.1 C in the range of 1.7 to 2.7 V, in which a high capacity of 1399.8 mAh g$^{-1}$ can be obtained. The typical plateaus at $\pm$ 2.35 and 2.12 V in the discharge curve represent reduction of S$_8$ to Li$_x$S$_{n}$ (4 ≤ x ≤ 8) and transition from Li$_x$S$_4$ to Li$_2$S$_2$/Li$_3$S, respectively [8]. After fully discharged, the electrode was charged to 2.7 V and a long charging plateau was found in the charging curve of approximately 2.2 to 2.35 V. The plateau is associated with the oxidation processes involving the overall consumption of Li$_2$S$_n$ (1≤ n≤ 8).

As shown in Figure 3b, we have also studied rate performance to understand the electrochemical behavior of NiCo$_2$O$_4$ based cathode. As the current density increases from 0.2 C to 1.0 C (0.2 ,0.5 ,0.7 ,1.0 C), the cell shows a good rated with average discharge capacities of 972, 946.7, 767, and 544.6 mAh g$^{-1}$, respectively, indicating that the exclusively designed NiCo$_2$O$_4$ nanostructures has great potential as a high rate cathode material. Moreover, when the current density is again reduced to 0.2 C, the average discharge capacity of 764.3 mAh g$^{-1}$, can be recovered. Figure 3c shows cyclic performance of the electrode with NiCo$_2$O$_4$ at 0.5 C. After activation at 0.1 C for 3 cycles, the NiCo$_2$O$_4$ based electrode obtains a capacity of 692.5 mAhg$^{-1}$ after 59 cycles, then slowly decreased until it stabilized at 464.2 mAhg$^{-1}$ after 200 cycles.

To reveal the electrochemical mechanism, the CV curves of the NiCo$_2$O$_4$ electrode at rates of 0.3, 0.5 and 0.7 mV s$^{-1}$ in the potential range of 1.7 ~ 2.7 V (vs. Li/Li$^+$) are shown in Figure 3d. Two cathodic peaks of about 2.2 and 1.9 V can be observed, associated to formation of soluble high-order polysulfides (Li$_3$S$_n$, 4 ≤ x ≤ 8) from sulfur and conversion of long-chain polysulfides to Li$_2$S$_2$/Li$_3$S, respectively. A sharp anodic peak can be observed at about 2.5 V, which can be assigned to
transformation from Li$_2$S$_2$/Li$_2$S to S [9]. Combing the linear relationship between peak current and square root at different scan rate, the Li$^+$ diffusion coefficient of peaks at 2.5, 2.2 and 1.9 V in the NiCo$_2$O$_4$ based battery are calculated to be $0.9 \times 10^{-7}$, $0.1 \times 10^{-7}$ and $0.5 \times 10^{-7}$ cm$^2$ s$^{-1}$, respectively, based on the Randles-Sevcik equation, indicating facilitated ionic transport due to the porous nanostructures [9].

![Figure 3](image)

**Figure 3.** Electrochemical performances of the NiCo$_2$O$_4$/sulfur composites electrode. (a) The discharge/charge profiles. (b) Rate capability. (c) Cycle performance at 0.5 C. (d) CV curves at different scan rate.

4. Conclusions
In this study, NiCo$_2$O$_4$ nanoparticles was prepared via a facile atmospheric and water-based method and designed as cathode additive for Li-S batteries. The mesoporous NiCo$_2$O$_4$ nanoparticles can provide abundant adsorption sites to confine polysulfides and facilitate the ionic transport. As a result, the cells with NiCo$_2$O$_4$ nanoparticles show an initial specific capacity of 1399.8 mAh g$^{-1}$ at the current density of 0.1 C and reversible high rate performances. This work may provide a promising method for preparing high-performance cathodes of Li-S batteries.

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