RESEARCH ARTICLE

Electrochemical study of graphene oxide and Co_3O_4 nanocomposite as an anode material for long-life lithium-ion batteries

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Received: June 26, 2023; **accepted:** August 7, 2023.

Lithium batteries, as a type of advanced battery technology, have extremely high application value. However, lithium-ion batteries are prone to aging and malfunction after prolonged charging and discharging, which affects their performance. The correct selection of electrode materials can improve the service life of lithium-ion batteries. In order to optimize the electrochemical materials of lithium-ion batteries, this study conducted electrochemical analysis on graphene oxide (GO) and Co_3O_4 (GO/Co_3O_4) nanocomposites used as anodes of long-acting lithium-ion batteries. The GO/Co_3O_4 nanocomposites were synthesized by using hydrothermal method, and the properties of GO/Co_3O_4 nanocomposites were analyzed. X-ray diffraction (XRD) analysis showed that Co_3O_4 nanoparticles were uniformly formed on the surface of GO nanosheets. The GO/Co_3O_4 nanocomposite electrode had 50% by weight (wt) of Co_3O_4 according to electrochemical characterizations of the GO, Co_3O_4, and GO/Co_3O_4 electrodes in lithium-ion batteries. The capacity was found to increase when the Co_3O_4 content was increased to 50% of the sample, while the capacity decreased as Co_3O_4 concentration increased. The GO/Co_3O_4 nanocomposite electrode that contained 50 wt% Co_3O_4 exhibited excellent cyclic stability, delivering more than 1,115 mA h/g at a current density of 0.1 A/g with minimal capacity loss, a Coulombic efficiency that approached almost 99.5% over 500 cycles, and good capacity retention (95%). Therefore, GO/Co_3O_4 nanocomposite could be an appropriate electrode material with improved cycling stability. The results of this study provided a good direction for the optimization of electrode materials and electrochemical research in lithium batteries.

Keywords: graphene oxide; Co_3O_4 nanoparticles; GO/Co_3O_4 nanocomposites; lithium-ion batteries; long-life; rate capability; cycling stability; capacity retention.

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Introduction

The application of lithium ions in its electrochemistry distinguishes a lithium-ion battery as an advanced battery technology. During discharge cycles, the lithium atoms in the anode go through ionization and become separated from their electrons. These ionized lithium ions then traverse through the electrolyte and merge with their electrons once more at the cathode, resulting in electrical neutrality [1]. Their minuscule size allows them to pass effortlessly through a micro-permeable barrier that divides the anode from the cathode. Lithium-ion batteries deliver remarkable voltage and charge storage per unit mass and unit volume, which is attributed, in part, to the compactness of lithium. Most portable consumer gadgets including mobile phones, laptops, power tools, life-saving medical equipment, personal mobility scooters, digital cameras, and electric cars employ lithium-ion batteries as rechargeable batteries for devices. The lithium-ion battery is of particular relevance as it boasts the highest

charge-to-weight ratio, which is crucial for batteries used in transportation applications. Moreover, lithium is the least vulnerable metal to substitution [2]. Notwithstanding its overall advantages, lithium-ion batteries do have certain drawbacks such as fragility and requiring a protection circuit to function safely. Lithium-ion batteries can age, which causes them to lose capacity and frequently malfunction after years. As a result, additional research is required to enhance energy density, operation safety, and lifespan, all of which primarily depend on the electrode materials [3].

Graphite has been suggested as a commercial anode material on the anode side because of its unmatched combination of abundance and relatively low cost. However, due to its finite theoretical capacity of 372 mAh/g and the performance limitations of contemporary lithium-ion batteries, it is insufficient to fundamentally alter applications that involve high-energy battery systems [4, 5]. Numerous studies on improving the performance of lithium-ion batteries showed that using an electrode with a nanostructure could increase capacity, rate characteristics, and lifespan [5-10]. When carbon nanotubes (CNTs), graphite oxide, carbon-based nanocomposites, and other innovative carbon structures were used as anode materials, they had high capacity and environmental protection. Among them, graphite oxide was widely concerned because it could control the conductivity of materials by controlling the degree of oxidation. Compared with single graphene, graphite oxide electrode material could control the battery capacity more accurately. Therefore, at present, graphene is often used in the research of material strength and electronics, while graphite oxide is often used in energy storage [11-15]. Co_3O_4 is widely used in battery materials due to its excellent conductivity and large battery capacity and has high application value. Meanwhile, the Co_3O_4 electrode material can be recycled for a long time during the charging and discharging process, and this process does not generate excessive pollutants and energy consumption, which has certain environmentally friendly performance.

This study investigated graphene oxide (GO) and Co_3O_4 nanocomposite electrochemically as an anode material for long-lasting lithium-ion batteries. In order to improve the service life of lithium batteries, this study considered the optimization direction of electrode materials by synthesis of GO/Co_3O_4 nanocomposites, and then explored the electrochemical properties of this material to prove its feasibility as an electrode anode material. The results of this study would provide some directions for the optimization of electrode material performance in the battery industry.

Materials and Methods

Synthesis of GO/Co_3O_4 nanocomposite material

Hydrothermal method was used for synthesis of GO/Co_3O_4 nanocomposite material [16]. Briefly, 200 mL of 4 mg/mL graphene oxide (GO) (99%) (Yuanye Biotechnology Co., Ltd., Shanghai, China) suspension was ultrasonically dispersed for 35 minutes at 25°C by using Scientz-1500F ultrasonic disperser (Chengzao Instrument Equipment Co., Ltd., Shanghai, China). Then, 1.2 g of $Co(NO_3)_2 \cdot 6H_2O$ (99%) and 1.5 g of CH_4N_2O (98%) (Sigma Aldrich (Shanghai), Shanghai, China) were added into the GO suspension and mixed for 40 minutes. The mixture was then heated in JC-STSX30L Autoclave (Juchuang Century Environmental Protection Technology Co., Ltd., Qingdao, Shandong, China) for 10 hours at 115°C to synthesize nanocomposite. The synthesized nanocomposite was then washed three times with deionized water after cooling down from autoclave by centrifugation at 8,000 rpm for 10 minutes at room temperature. After wash, the nanocomposites were freeze-dried by using FD-1A-50 freeze-drying machine (Shunzhi Instrument Manufacturing Co., Ltd., Shanghai, China) at -40°C for 60 minutes. For comparison, the same process was performed to produce pure Co_3O_4 nanostructures without the addition of GO.

Table 1. The electrochemical act of GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4 in this study and reported anode materials used for lithium-ion batteries in literature.

Anodes	Voltage-range (V)	Discharge-capacity (mA h/g)	Coulombic efficiency (%)	Ref.
Co_3O_4/MWCNTs nanocable	0.00–3.0	1109 (0.89 A/g)	99% (250 cycles) at 0.89 A/g	[8]
Co_3O_4/Co @ N-doped CNTs	0.01-3.0	689.2 (0.5 A/g)	95% (400 cycles) at 0.5 A/g	[7]
N-doped CN @ Co-Co_3O_4/CNTs composite	0.01-3.0	460 (5 A/g)	98% (300 cycles) at 5 A/g	[6]
Co_3O_4/CNTs nanocomposite	0.01–3.0	873 (0.1 A/g)	97% (50 cycles) at 0.1 A/g	[17]
Hierarchical porous MWCNTs/Co_3O_4 nanocomposites	0.00–3.0	813 (0.1 A/g)	95% (100cycles) at 0. 1A/g	[18]
Co_3O_4/graphene/CNTs	0.00–3.0	185 (1.6 A/g)	99% (55 cycles) at 1.6 A/g	[19]
GO/Co_3O_4 nanocomposite contained 50 wt% Co_3O_4	0.001–3.0	1115 (0.1 A/g) 952 (0.5 A/g) 825 (1 A/g) 667 (2 A/g) 513 (4 A/g)	99.5% (500 cycles) at 0.1 A/g	This study

Characterization of electrochemical properties of GO/Co_3O_4 nanocomposite

The electrochemical characterization of the GO/Co_3O_4 nanocomposite in lithium-ion batteries was explored by using a galvanostatic charge/discharge measurements in the voltage window of 0.001 - 3.0 V vs Li/Li^+ at different current densities. The information and sources of the electrode materials used in the experiments were shown in Table 1 [6-8, 17-19]. The lithium-ion battery cells were coupled to HJ1020mSD8 battery charge-discharge system (Hokuto Denko Corp., Tokyo, Japan) for galvanostatic charge/discharge measurements. The experimental process involved removing the charging switch wiring of the lithium-ion battery, adjusting the voltage of the discharge instrument to different ranges of 0.001 to 3.0 V, recording the battery current and temperature changes under different states, and calculating the efficiency of the lithium-ion battery. The tested GO/Co_3O_4 nanocomposite material was calcined at 1,000°C for 30 minutes in HR-B1000 high-temperature furnace (Huarong Kiln Co., Ltd., Luoyang, Henan, China), cooled down naturally at room temperature, and then cleaned with acid solution and dried to obtain lithium battery anode material.

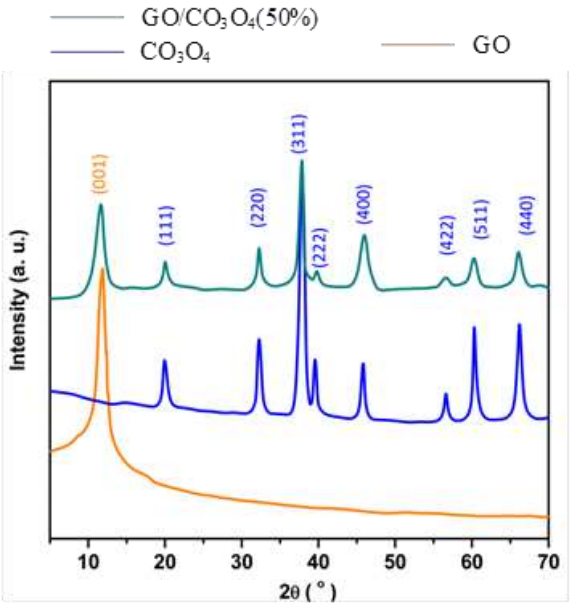

Figure 1. XRD spectra of GO, Co_3O_4, and GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4.

Results and discussion

XRD spectra of GO, Co_3O_4, and GO/Co_3O_4 nanocomposite

The XRD spectra of GO, Co_3O_4, and GO/Co_3O_4 nanocomposite contained 50 wt% Co_3O_4 were shown in Figure 1. It was observed that there was a strong diffraction peak in the XRD spectra of GO

specimen at 2θ = 11.88°, which indicated the crystallographic reflection of GO structure [20], while the XRD spectra of Co_3O_4 and GO/Co_3O_4 nanocomposite showed characteristic diffraction peaks at 2θ = 20°, 31°, 37°, 39°, 45°, 59°, and 65°, which represented the crystallographic reflections of face centered cubic spinel phase of Co_3O_4 (JCPDS card No. 00-042-1467) [21]. The XRD spectra of GO/Co_3O_4 displayed an additional GO peak that indicated the presence of the GO nanosheets in nanocomposite structure [22-26].

The potential profiles of GO, Co_3O_4, and GO/Co_3O_4 nanocomposite

The potential profile of the GO, Co_3O_4, and GO/Co_3O_4 nanocomposite electrode during the first lithium addition and extraction cycle with a potential window of 0.001 to 3.0 V at room temperature and a current density of 0.1 A/g was shown in Figure 2 [27-29]. The first charge-discharge profiles of Co_3O_4 and GO/Co_3O_4 nanocomposite electrodes demonstrated a wider potential plateau at around 1.12 V, indicating that lithium combined with Co_3O_4 during the first discharge to generate Li_2O and cobalt metal [30, 31]. The slope that developed throughout the charging procedure in the range of 1.2 to 2.0 V represented a reversible oxidation reaction [32], which corresponded to the straight rising line of the charge profile of the Co_3O_4 electrode. The results indicated that the Columbic efficiency of GO, Co_3O_4, and GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4 were 94%, 78%, and 99%, respectively. The production of solid–electrolyte interphase (SEI) passivation film as a result of the electrolyte breakdown at the electrode/electrolyte interface was most likely what caused the majority of the capacity loss [33]. The GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4 showed the highest value of reversible capacity (1,115 mA h/g at a current density of 0.1 A/g). Figure 3 showed that, with the increase of current density to 4 A/g, the specific capacity of GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4 demonstrated the trend of decrease and reached 513 mA h/g at 4 A/g, reflecting an excellent performance rate of GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4.

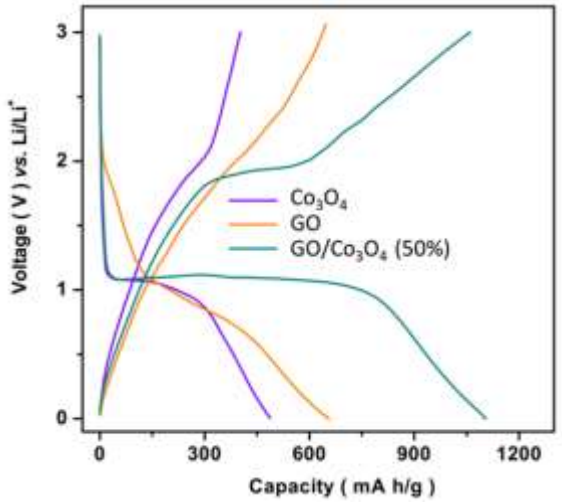

Figure 2. The potential profiles of GO, Co_3O_4, and GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4 at the potential widow of 0.001 to 3.0 V at room temperature and a current density of 0.1 A/g during the first lithium insertion and extraction cycle.

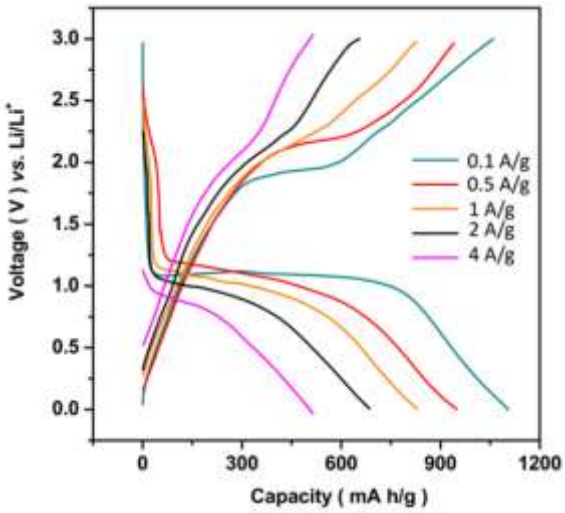

Figure 3. The potential profile of GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4 at different current densities.

The effects of Co_3O_4 concentrations on the cyclic stability of GO/Co_3O_4 nanocomposite electrode

The cyclic stabilities of GO/Co_3O_4 nanocomposite electrodes with the different concentrations of Co_3O_4 in the GO/Co_3O_4 at 20%, 40%, 50%, and

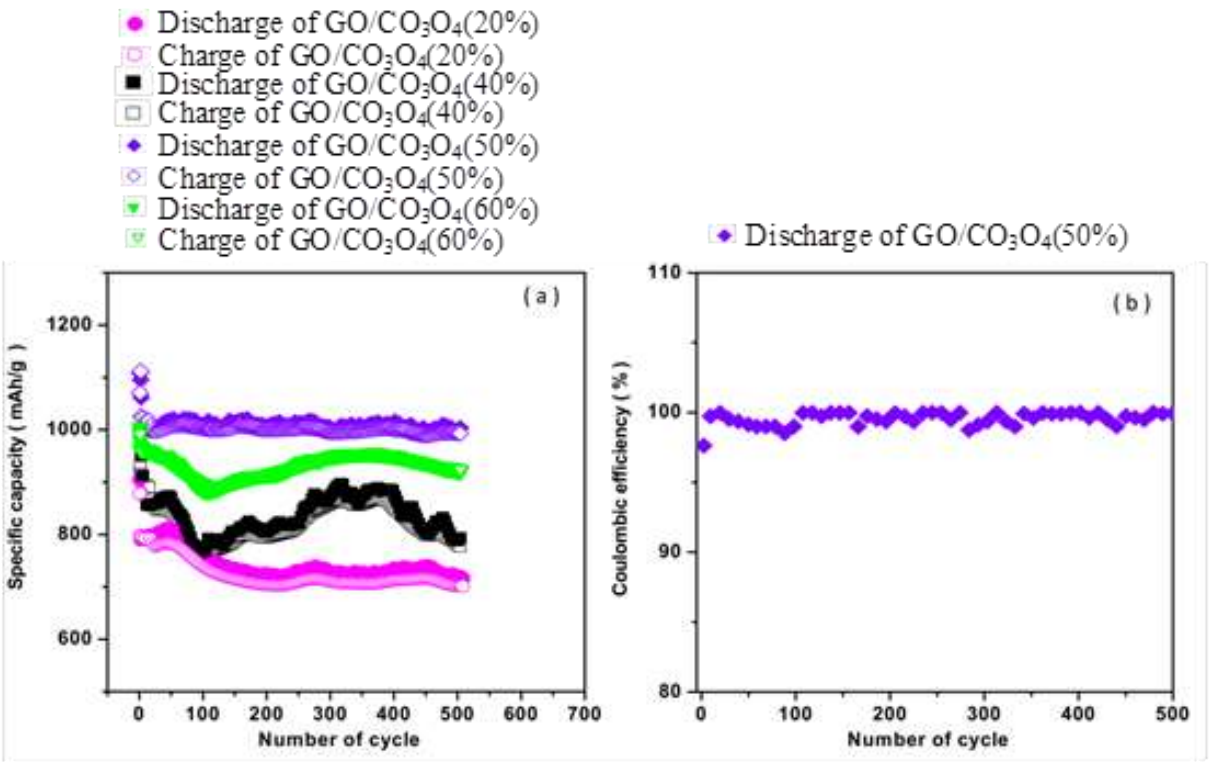

Figure 4. The cyclic stability of GO/Co_3O_4 nanocomposite electrodes with different concentrations of Co_3O_4 in GO/Co_3O_4 at 20%, 40%, 50%, and 60% at the current density of 0.1 A/g (a) and Coulombic efficiency of GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4 at the current density of 0.1 A/g (b).

60% were tested at the current density of 0.1 A/g. As shown in Figure 4a, increasing the Co_3O_4 concentration to 50% in the sample caused an increase in capacity, while increasing the concentration of Co_3O_4 to 60% caused a decrease in capacity. The results indicated the massive volume expansion-contraction and severe particle aggregation, which could cause irreversible capacity fading, a short cycle life, and deteriorated electric contact between particles [34, 35]. The GO/Co_3O_4 nanocomposite electrode contained 50 wt% Co_3O_4 electrode exhibited great cyclic stability more than 1,115 mA h/g with negligible capacity loss and a Coulombic efficiency approaching almost 99.5% over 500 cycles (Figure 4b) and good capacity retention (95%). Therefore, GO/Co_3O_4 nanocomposite could be an appropriate material for electrode with improved cycling stability.

Conclusion

Graphene oxide (GO) and Co_3O_4 nanocomposite had been studied electrochemically as an anode material for long-lasting lithium-ion batteries. In GO/Co_3O_4 nanocomposite materials, Co_3O_4 nanoparticles were uniformly formed on the surface of GO nanosheets. The XRD study of the structural properties of GO/Co_3O_4 nanocomposite electrodes demonstrated the strong interaction/contact between GO nanosheets and Co_3O_4 nanoparticles. The results of this study also showed that the capacity increased with a sample's Co_3O_4 content reaching 50% and decreased with a higher concentration of Co_3O_4, which indicated that severe particle aggregation and large volume expansion-contraction could result a significant amount of irreversible capacity fading, a short cycle life, and deteriorated electric contact between particles. The 50 wt% Co_3O_4 in the GO/Co_3O_4

nanocomposite electrode had excellent cyclic stability, delivering more than 1,115 mA h/g with little capacity loss, a Coulombic efficiency of over 99.5% over 500 cycles, and strong capacity retention (95%). Therefore, GO/Co_3O_4 nanocomposite could be an appropriate electrode material with improved cycling stability.

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