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Improvement in electrochemical performance of calcined $LiNi_{0.5}Mn_{1.5}O_4$/GO

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ABSTRACT

This study aimed to use the excellent properties of graphene as coating for the cathode material $LiNi_{0.5}Mn_{1.5}O_4$. In this work, we added a calcination process based on the graphene oxide coating process from previous studies to obtain the calcined $LiNi_{0.5}Mn_{1.5}O_4$/GO composite. The morphology and structure of the prepared samples were characterized by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. Their performance as electrodes of lithium-ion battery was investigated by charge/discharge and cycle performance tests. The calcined $LiNi_{0.5}Mn_{1.5}O_4$/GO composite obtained by the improved method presented a thin, compact, and uniform coating layer and improved the electrochemical performances of $LiNi_{0.5}Mn_{1.5}O_4$ with no effect on the crystal structure. The calcined $LiNi_{0.5}Mn_{1.5}O_4$/GO could deliver a capacity of 131.2 mAh g^{-1}, which was approximately 10 mAh g^{-1} larger than that of $LiNi_{0.5}Mn_{1.5}O_4$. After 280 cycles at 1 C rate, the calcined $LiNi_{0.5}Mn_{1.5}O_4$/GO could still deliver a reversible capacity of 123.2 mAh g^{-1}, retaining 94% of its initial reversible capacity.

1. Introduction

As the energy crisis has been becoming increasingly serious, traditional nonrenewable resources such as coal, petroleum, natural gas, and other fossil fuels can no longer satisfy human needs. The emergence of sustainable and renewable energy resources promotes the research and development of energy storage systems. As a form of energy storage, lithium-ion batteries with high energy density, long cycle life, low self-discharge rate, and environmental friendliness play important roles in the areas of notebook computers, mobile phones, digital cameras, and other electronic devices. However, as an energy storage system for electric vehicles and hybrid electric vehicles [1,2], lithium-ion batteries are required to have high energy density, long cycle life, and superior security [3,4]. Nevertheless, the electrochemical properties of lithium-ion batteries depend on cathode materials. Compared with other cathode materials, such as layered $LiCoO_2$, olivine $LiFePO_4$, and spinel $LiMn_2O_4$ [5,6], spinel $LiNi_{0.5}Mn_{1.5}O_4$ with high discharge voltage (approximately 4.7 V vs. Li/Li^+) [7], long cycle life, good safety, and low production cost is identified as one of the most promising cathode materials [8,9].

$LiNi_{0.5}Mn_{1.5}O_4$ was first researched when people discovered the substitution of the parent spinel $LiMn_2O_4$ with other metal ions (e.g., Co^{3+}, Ge^{4+}, Zn^{2+}, and Ni^{2+}) for Mn cations [10–13]. $LiNi_{0.5}Mn_{1.5}O_4$ possesses the advantages of $LiMn_2O_4$ and can inhibit the Jahn–Teller distortion in spinel $LiMn_2O_4$. However, the capacity still fades continuously during cycles because of the side reactions at the electrode/electrolyte interface, leading to irreversible destruction of the structure of $LiNi_{0.5}Mn_{1.5}O_4$ material at the high voltage of 4.7 V (vs. Li/Li^+) [14–16]. To solve these shortcomings, many strategies have been developed. Surface modification is one of the most direct and effective approaches, which can effectively prevent materials from direct contact with the electrolyte and greatly improve the electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$. To date, many materials have been successfully applied to coat the surface of $LiNi_{0.5}Mn_{1.5}O_4$, such as pure metal (e.g., Au [17] and Ag [18]), metal oxide (e.g., ZnO [19], ZrO_2 [20], and TiO_2 [21]), metal fluoride (e.g., AlF_3 [22]), or phosphate (e.g., Li_3PO_4 [23]). Most of the abovementioned materials are inactive substances that only function as protection shells, which increase electron and ion impedance and reduce the rate performance of $LiNi_{0.5}Mn_{1.5}O_4$ [24]. Svetlana Niketic et al. [25] reported that the carbon layer coated from Xerogel carbon (5 nm) is thinner than that coated from sucrose (10 nm) and greatly improves the electrochemical properties of $LiNi_{0.5}Mn_{1.5}O_4$. Thus, electro-conductive materials are new hotspots in terms of surface modification; the coating layers must be thin, highly compact, and sufficient. However, problems such as complex process and high cost limit studies on carbon-coated $LiNi_{0.5}Mn_{1.5}O_4$.

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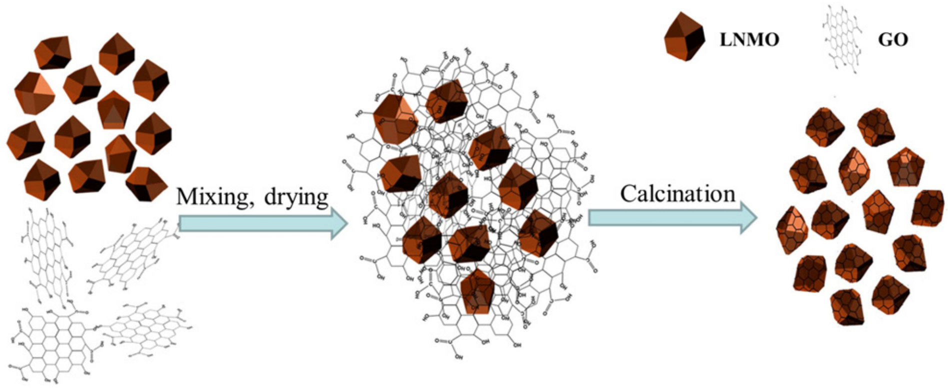

Fig. 1. The schematic illustration of the $LiNi_{0.5}Mn_{1.5}O_4$ coated process.

In recent years, graphene and graphene oxide (GO) have been reported to improve the electrochemical performance of many cathode materials for lithium-ion batteries because of their large specific surface and good electrical conductivity. Previous studies reported that modified GO and graphene can improve the electrochemical performance of spinel $LiNi_{0.5}Mn_{1.5}O_4$ [26], olivine $LiFePO_4$ [27], $LiNi_{0.5}Mn_{1.5}O_4$ nanorods [28], and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ [29] cathodes of lithium-ion battery by enhancing conductivity and protecting the cathode surface from undesired reactions with the electrolyte. However, as a modifying material directly coated to the surface of cathode materials, non-hydrophilic graphene can accumulate and is difficult to disperse. The transmission electron microscopy (TEM) images of the $LiNi_{0.5}Mn_{1.5}O_4$-graphene composite reported by Xiao Tang et al. [28] show that most graphene is dispersed around $LiNi_{0.5}Mn_{1.5}O_4$ rather than coated on the surface of $LiNi_{0.5}Mn_{1.5}O_4$. After 200 cycles at 0.1 C rate, the $LiNi_{0.5}Mn_{1.5}O_4$-graphene electrode could deliver a reversible capacity of about 115 mAh g^{-1}, retaining 94% of its initial reversible capacity (122.4 mAh g^{-1}). GO with a large amount of oxygen-containing groups can closely coat onto the surface of $LiNi_{0.5}Mn_{1.5}O_4$ [26], but the electronic conductivity of GO is much lower than that of graphene. The Graphene-oxide-coated $LiNi_{0.5}Mn_{1.5}O_4$ achieved by Xin Fang et al. [26] just could deliever a reversible capacity of about 116 mAh g^{-1} at a current of 0.2 C. Graphene and GO coating cathode materials are still in their infancy, and further studies are necessary. In this work, we added a calcination process based on the GO coating of $LiNi_{0.5}Mn_{1.5}O_4$ from the literature [26]. The comparison of calcined and non-calcined samples showed that the coating layer modified on the outer surface of $LiNi_{0.5}Mn_{1.5}O_4$ became thinner, more compact, and uniform after calcination. The calcined $LiNi_{0.5}Mn_{1.5}O_4$/GO obtained in this study demonstrated superior electrochemical performance, exhibiting the outstanding electronic conductivity of graphene. A detailed comparison of the performances of $LiNi_{0.5}Mn_{1.5}O_4$, $LiNi_{0.5}Mn_{1.5}O_4$/GO composite, and calcined $LiNi_{0.5}Mn_{1.5}O_4$/GO composite was performed.

2. Experimental

2.1. Preparation of materials

$LiNi_{0.5}Mn_{1.5}O_4$ (named LNMO) was synthesized by the solid-state method [30]. Li_2CO_3, NiO, and Mn_3O_4 used in this study were A.R. grade, and the cationic mole ratio of Li:Ni:Mn was 1.03:0.5:1.5. Then, the chemical mixture was preheated at 600 °C for 5 h and calcined at 800 °C for 12 h. After naturally cooling to room temperature, the calcined product was grinded and subsequently sieved to obtain the final $LiNi_{0.5}Mn_{1.5}O_4$. GO was prepared by Hummers method from graphite powder [31]. To prepare the GO-coated LNMO, 4.0 g of as-prepared LNMO was added into uniformly dispersed GO solution (0.8 g of GO dispersed in 60 mL of anhydrous ethanol) and then mixed by stirring and ultrasonication. The obtained mixture was evaporated to dryness at 90 °C and dried at 120 °C for 3 h in a vacuum to obtain the $LiNi_{0.5}Mn_{1.5}O_4$/GO composite (named GO-LNMO). Subsequently, part of the GO-LNMO was sintered at 400 °C for 3 h in air to obtain the calcined $LiNi_{0.5}Mn_{1.5}O_4$/GO composite (named CGO-LNMO) [32,33,34], as shown in Fig. 1.

2.2. Physical characterization

The crystal structure of the as-prepared samples were characterized by powder X-ray diffraction (XRD, Rigaku D/max-2000) with monochromated Cu Kα radiation (40 kV, 20 mA). The scanning range of 2θ was from 10° to 80°. The particle size and the morphology of materials were observed by using a scanning electron microscope (SEM, FEI Quanta FEG 250) and transmission electron microscopy (TEM, JEM-2100HR).

2.3. Electrochemical tests

The as-prepared LNMO or GO-LNMO or CGO-LNMO, carbon black and polyvinylidene fluoride (PVDF) were mixed with a weight ratio of 8.5:0.75:0.75 in N-methyl pyrrolidinone and coated onto aluminum foil to fabricate the cathodes. The cathodes were dried at 120 °C

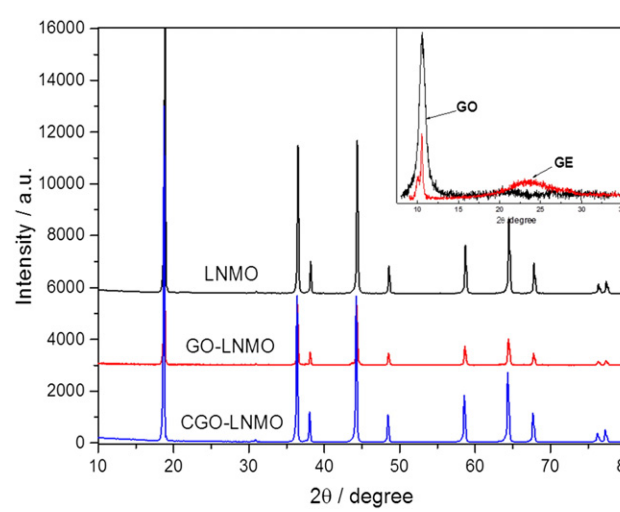

Fig. 2. XRD patterns of as-synthesized LNMO, GO-LNMO, CGO-LNMO, the pristine graphene oxide and the calcined graphene oxide.