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Graphene-analogous structural MoS_2 modification to improve electrochemical properties of Ni-rich layered oxide cathode material for lithium-ion batteries

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HIGHLIGHTS

- MoS_2 is successfully introduced to modify Ni-rich layered oxide cathode material.
- MoS_2 coating layer works as protective barrier and charge transfer tunnel.
- MoS_2-modified cathode material exhibits outstanding electrochemical properties.
- Mechanism investigation for the MoS_2 modification is provided.

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ABSTRACT

Ni-rich cathode material attracts a substantial amount of attention due to its high specific capacity, superior energy density and low cost. Nonetheless, there are still a few intrinsic issues which need to be solved including rate performance, cycling stability, elevated-temperature performance, etc. In this paper, the graphene-analogous structural MoS_2 with chemical stability and acceptable conductivity is purposefully introduced to modify $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode material via a facile wet-chemical approach followed by low-temperature reaction. In addition, lithium-active MoS_2 coating layer can provide an interconnected and stable tunnel for the insertion and extraction of lithium ions. Characterizations by X-ray diffraction, X-ray photoelectron spectroscopy, Raman, scanning electron microscopy and transmission electron microscopy demonstrate that MoS_2 coating layer is uniformly deposited on the surface of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ material. The electrochemical results indicate that the modified cathode material displays excellent structure stability, superior rate performance and outstanding cycling properties.

1. Introduction

Lithium-ion batteries have been broadly applied in electronic devices, and are gradually expanding to electric vehicles and efficient energy storage power stations. At present, nickel-rich layered oxide $LiNi_xCo_yMn_{1-x-y}O_2$ ($x > 0.6$) is considered as promising cathode material for the next generation of lithium-ion batteries owing to the superiorities of low cost, high specific capacity and superior energy density [1–4]. Nevertheless, there are still a few intrinsic issues to be resolved for the nickel-rich material. First, surface residual lithium of nickel-rich material can prone to reacting with water and carbon dioxide in the air. The reaction mechanism is shown below [5]. $O^{2-} + CO_2/H_2O \rightarrow CO_3^{2-}/2OH^-$, $Li^+ + CO_3^{2-}/2OH^- \rightarrow Li_2CO_3/2LiOH$. This process will lead to the surface deoxidization of nickel-rich cathode material and form a distorted surface oxide layer. Moreover, the decomposition of Li_2CO_3 on the surface of nickel-rich cathode material is a major cause of the battery gas expansion, which results in security concerns. Second, the dissolution of the nickel, cobalt and manganese transition metals from electrodes into liquid electrolyte owing to the corrosion of hydrogen fluoride (HF) produced by the decomposition of the electrolyte, which will migrate to the surface of the negative electrodes and cause the destruction and reconstruction of SEI film, thus accelerating the expenditure of active lithium [6]. Third, during the charge-discharge process of lithium-ion batteries, the structure of positive electrode active material will be destroyed accompanied by the occurrence of some side reactions, which leads to the

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continuous increase of the internal resistance and therefore lowered the specific discharge capacity [7]. Substantial investigation has been proved that surface modification is an effective way to solve the aforementioned problems. The surface modification material can be generally divided into oxide and non-oxide, such as Al_2O_3 [8], Co_3O_4 [9], $Ni_3(PO_4)_2$ [10], Li_2ZrO_3 [11], xLi_2O-yB_2O_3-zLiF [12]. These modification materials have been effectively demonstrated to improve the electrochemical performance of host material.

Transition metal sulfides, especially molybdenum disulfide (MoS_2), have been extensively researched because of its outstanding chemical stability, acceptable conductivity and steady layer structure [13–15]. In addition, MoS_2 is also a layered two-dimensional structure similar to the graphene and it's an A-B-A sandwich layered structure consisting of two S layers and one a Mo layer, which the adjacent layers interact by van der Waals force. This characteristic structure can provide an interconnected and stable tunnel for the insertion and extraction of lithium ions [16–18]. In this paper, we have adopted graphene-analogous structural MoS_2 to modify $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM) material. Such a modified strategy has the following three roles: (1) MoS_2 with chemical stability can act as a protective layer to enhance the interfacial stability and decrease the side reactions, resulting in the improvement of structure stability; (2) the introduction of MoS_2 with acceptable conductivity can enhance charge transfer of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode material, leading to an increase in the rate capability; (3) the formation of a uniform MoS_2 coating layer with providing additional lithium-ions de/intercalation sites can decrease the irreversible specific capacity loss, thereby improving the initial coulombic efficiency.

2. Experimental

2.1. Preparation of the material

The MoS_2-modified $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM, 0.39 $m^2 g^{-1}$, Brunp, Guangdong) material was synthesize via a liquid phase method and solid state reaction. 0.41 g Ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$, 99.99%, Jingkang, Changsha) was dispersed into ethanol solution by magnetic stirring. Then, 10 g NCM powders were immersed in the above dispersion, and kept stirring in a constant temperature bath of 60 °C until the ethanol solvent was completely evaporated. The acquired gel was dried at 100 °C for overnight in a vacuum oven and then calcined at 500 °C for 5 h under an argon atmosphere to get the MoS_2-modified $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM) sample, abbreviated as NCM@MoS_2. And the amount of the MoS_2 corresponding to NCM was designed in a mass ratio of 2.5%. Schematic diagram for the synthesis of NCM@MoS_2 was illustrated in Fig. 1.

2.2. Material characterizations

X-ray diffraction (XRD, Rigaku TTRIII) was employed to determine the crystalline phases of the prepared powders with the 2θ range of 10–80° at a scanning rate of 10°/min. Surface element analysis was carried out by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi). Raman spectra were performed on the Renishaw Raman instrument (InVia Raman Microscope) with the green laser light of 532 nm. Scanning electron microscopy (SEM, Nova NanoSEM230) with an energy dispersive spectrum X-ray detector (EDS) was adopted to examine the surface morphologies and elemental mapping of the synthesized samples. Transmission electron microscopy (TEM, Titan G2 60–300) was used to analyze the microstructure of the prepared samples. The fabricated coin-cells were charged to 4.3 V and then unpacked in a glove box with high-purity argon, the acquired electrodes were soaked in the liquid electrolyte under 55 °C. Inductively coupled plasma (ICP) test was performed to measure the dissolved quantity of transition metals from electrodes into liquid electrolyte.

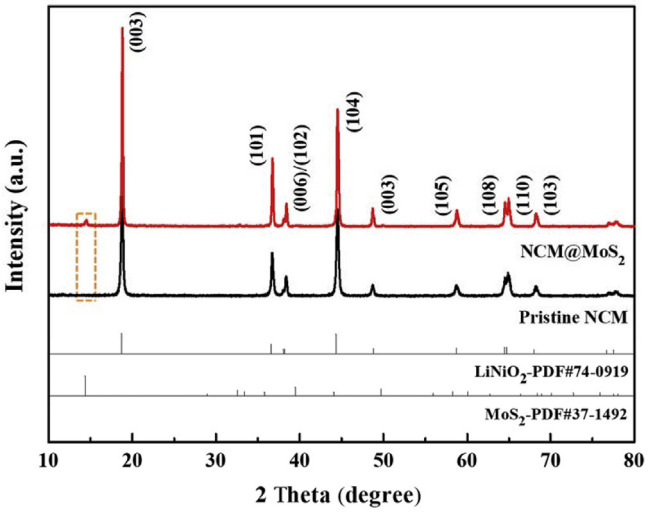

Fig. 2. XRD patterns of the pristine NCM and NCM@MoS_2 samples.

2.3. Electrochemical evaluation

Positive electrodes were prepared by blending 80 wt% $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (active material), 10 wt% acetylene black and 10 wt% poly (vinylidene fluoride) (PVDF) binder in N-methylpyrrolidinone (NMP) solvent. The acquired active mass was uniformly cast onto aluminum foil and then dried at 120 °C for 12 h in the vacuum oven to remove NMP solvent or absorbed moisture. CR2025 cells were assembled in the argon-filled vacuum glove box. A lithium metal foil was used as the negative electrode, a Celgard2400 porous polypropylene film was employed as the separator to avoid short circuits and make ions pass through. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC)/ethylene carbonate (EC) at a 1:1:1 vol ratio. The electrode mass loading

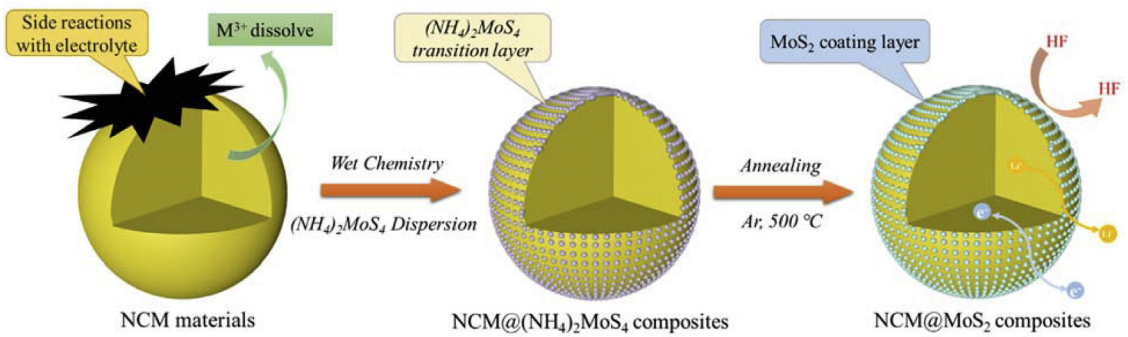

Fig. 1. Schematic diagram for the synthesis of NCM@MoS_2 material.