



Enhanced electrochemical performance of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ by surface modification with graphene-like lithium-active MoS_2



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ABSTRACT

In order to improve the high-rate capacity and cycleability, the graphene-like structured MoS_2 is successfully coated on $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ via wet chemical method followed by a solid state reaction. Transmission electron microscopy and energy dispersive X-ray spectrometry indicate that the surface of cathode particles is uniformly covered with a crystalline MoS_2 layer (~ 5 nm thick) after 3 wt% MoS_2 surface coating. Compared with the bare sample, MoS_2 -coated electrode exhibits the improved Coulombic efficiency, cycleability and rate capability in the voltage range of 2.0–4.8 V, even at elevated temperature. Based on the analysis from cyclic voltammetry and electrochemical impedance spectra, the remarkably improved electrochemical performances of the surface-modified electrode are ascribed to the presence of lithium-active MoS_2 coating with the layered structure, which could not only suppress the undesirable side reaction and increasing impedance, and enhance the structural stability of host material, but also provide the additional sites for insertion of extracted lithium to compensate the lost Li sites during the activation of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ to effectively increase the initial Coulombic efficiency.

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1. Introduction

Recently, as a kind of the layered lithium transition metal oxides which have been extensively investigated as cathode materials in the next generation of the rechargeable lithium-ion batteries (LIBs) [1,2], Li-excess Mn-based ones represented as $\text{Li}[\text{Li}_{(1/3-2x/3)}\text{M}_x\text{Mn}_{(2/3-x/3)}]\text{O}_2$, equivalently $y\text{Li}_2\text{MnO}_3 \cdot (1-y)\text{LiMO}_2$ ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{etc.}$), have some advantages such as lower cost, less toxic and safer on overcharge than the widely used layered LiCoO_2 and ternary cathode material with $\alpha\text{-NaFeO}_2$ structure [3–5]. Li-excess Mn-based cathodes with high capacities of $\sim 250 \text{ mAh g}^{-1}$ at high voltages can supply excess lithium to the layered structure that plays a critical role in stabilizing the electrode structure [4,6]. However, there are still several practical problems for their commercial application, e.g. low Coulombic efficiency, poor rate

capability and cyclic performance [7–9]. Surface modification by coating with the inert/active materials is demonstrated to be an effective and simple method for improving the high-rate capability and Coulombic efficiency of the Li-excess Mn-based cathode. Many inorganic compounds, such as metal oxides [10–12], fluorides [8,13] and phosphates [14,15], have been reported as the surface-coating materials, which could be divided in to the inert and active materials. The inert or inactive coating layers can improve the electrochemical properties of Li-excess Mn-based cathodes as the protective materials against corrosion from electrolyte [8,10,11,13,14]. However, surface modifications with the electrochemically inactive materials would decrease the energy and volumetric densities of the active cathode materials and affect the lithium ion and electron transfer in working electrodes [15,16]. Usually, the active coatings, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [12], LiCoPO_4 [15], can provide a number of available sites for the insertion of extracted lithium.

Layered transition metal disulfides TMS_2 such as MoS_2 have been used as the novel anode materials of LIBs [17,18], owing to their analogous structure similar to the graphite and graphene, in

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which a Mo layer sandwiched between two S layers, and these triple layers are stacked and held together by van der Waals force [19]. Due to the weak van der Waals interactions, Li-free MoS₂ with the graphene-like structure enables the convenient insertion and extraction of Li⁺ ions from its layered structure without major volume expansion in its overall dimension [20–22]. It has been reported that the MoO₃ nanobelts coated with a thin layer of MoS₂ exhibit a perfectly reversible conversion plateau with a high Coulombic efficiency about 98% [23]. Meanwhile, MoS₂ in nano-shape is more stable than the transition metal oxide, due to its high conductivity, excellent chemical stability against electrolyte, and stable crystal structure during cycling [23]. Therefore, we consider the layered MoS₂ as a good candidate of the active surface coating materials for the layered cathode material, because Li-free MoS₂ would reduce the irreversible capacity loss of Li-excess Mn-based material during the first cycle by providing additional Li⁺ insertion sites.

Although layered MoS₂ exhibits many competitive advantages discussed above, surface modification of the layered cathode materials such as LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ with layered transition metal disulfide has not been reported yet. In this work, the electrochemically active MoS₂-coated Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ (LMNCO) sample are prepared via the thermolysis of (NH₄)₂MoS₄. And the structure, morphology and electrochemical properties of the cathodes are also investigated. Compared with the pristine one, the MoS₂-coated LMNCO shows the obviously improved Coulombic efficiency, high-rate discharge capability and cycleability.

2. Experimental

2.1. Preparation of MoS₂-coated Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂

First, Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ powder, as a pristine material, was prepared by combination of the carbonate co-precipitation and solid state reaction process [24,25].

MoS₂-coated LMNCO sample are prepared via the wet-chemical method followed by a solid state reaction. Ammonium tetrathiomolybdate ((NH₄)₂MoS₄) was added into the moderate ethanol aqueous solution. The as-prepared LMNCO powder was then immersed into above mixture. After continuous stirring, the as-produced gel was dried at 80 °C overnight in vacuum. The resulted solid was annealed at 550 °C for 2 h under Ar atmosphere to obtain the MoS₂-coated Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ powders, marked as MoS₂-coated LMNCO. And the designed amount of MoS₂ was 3 wt% of the layered Li-excess Mn-based oxide.

2.2. Materials characterization

X-ray diffraction (XRD) patterns were recorded by a diffractometer (D/max 2000, Rigaku) employing Cu K α radiation operated at 40 kV and 40 mA. The morphology and microstructure of the samples were examined using field-emission scanning electron microscope (FE-SEM, Ultra 55, Zeiss) coupled with an energy dispersive spectrum X-ray detector (EDS) and high-resolution transmission electron microscope (HR-TEM, Tecnai G² F20 S-Twin, FEI).

2.3. Electrochemical measurements

The slurry consisted of the active materials (80 wt%), carbon black (10 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) was casted on Al foil, and dried at 110 °C overnight in vacuum. 2025-type coin cells were assembled in an argon-filled glove box by using the metal lithium foil as the negative electrode, porous polypropylene film (Celgard 2500) as the separator, 1 M LiPF₆

dissolved in ethylene carbonate, and dimethyl carbonate (EC:DEC = 1:1, in weight) as the electrolyte.

The galvanostatical charge–discharge tests were performed at various current densities (1C = 250 mA g⁻¹) on a LAND battery program-control test system (Wuhan, China) in the potential window of 2.0–4.8 V range (vs. Li/Li⁺). Cyclic voltammetry (CV) tests were carried out on an electrochemical workstation (CHI 660D) at a scan rate of 0.1 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) was carried out by an electrochemical workstation (CHI 660E), where an AC voltage of 5 mV amplitude was applied in the frequency range of 0.01–100 kHz at the charge state of 4.4 V. And the obtained EIS spectra were then fitted by Z-view 2.0 software.

3. Results and discussion

3.1. Material characterization

Fig. 1 shows the XRD patterns of the bare LMNCO and MoS₂-coated LMNCO with Miller indices. For the diffraction peaks of the both materials, the weak peaks at $2\theta = 20^\circ\text{--}25^\circ$ can be indexed to the LiMn₆ cation arrangement that occurs in the transition metal layers of Li₂MnO₃ region with the monoclinic unit-cell C2/m [10]. And the other peaks can be identified as the hexagonal α -NaFeO₂ structure with space group R-3m [10,26]. As shown in Fig. 1, the obvious distinct splittings of the adjacent peaks (006)/(012) and (108)/(110) indicate that both samples have a typical layered structure. The integrated intensity ratios of $I_{(003)}/I_{(104)}$ are 1.34 and 1.53 for the bare and coated samples, respectively, indicating that both samples have well-ordered α -NaFeO₂ structure with limited cation mixing. In addition, no diffraction peaks for crystalline MoS₂ are observed in the corresponding XRD pattern due to the amorphous state and/or its low content.

The micro-morphologies of the bare LMNCO and MoS₂-coated LMNCO are exhibited by FE-SEM images in Fig. 2. For the bare sample, it can be seen that the spherical secondary particles with the average particle size of 3.0 μm are consisted of numerous primary grains (Fig. 2a). Besides, the surface of the uncoated LMNCO particle is coarse, and many pores exist on the surface of the primary particle. By comparison, the surface of the particles become smooth (Fig. 2b) after MoS₂ coating. And the pores are almost indistinguishable. Meanwhile, the primary grain turns much more regular after the coating and post-annealing process. Additionally, no distinct change of the particle size is observed after MoS₂ modification. The elemental composition is also

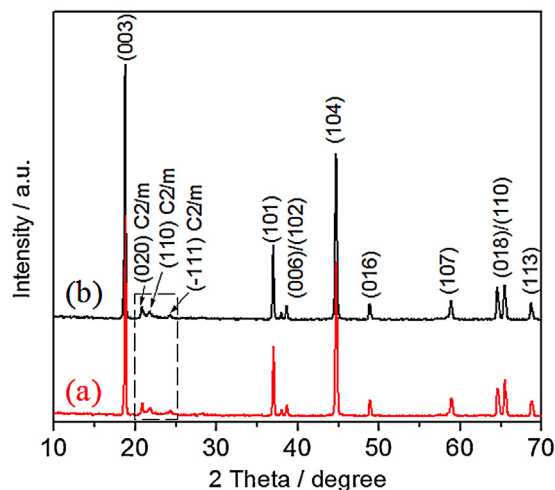


Fig. 1. XRD patterns of (a) bare LMNCO and (b) MoS₂-coated LMNCO powders.

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