Enhancing the electrochemical performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ by V$_2$O$_5$-modification for Li-ion batteries

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Abstract. The 2 wt.% V$_2$O$_5$-modified LiNi$_{0.5}$Mn$_{1.5}$O$_4$ material has been prepared by a sol-gel method. The as-prepared samples were characterized by XRD and SEM. XRD result shows V$_2$O$_5$-modification process did not destroy the structure of spinel LNMO. The electrochemical results show that the 2 wt.% V$_2$O$_5$-modified LiNi$_{0.5}$Mn$_{1.5}$O$_4$ sample exhibits a higher rate performance with discharge capacities of 133.3, 131.3, 129.8, 125.8, 120.1, 103.2, and 79.0 mAh g$^{-1}$ at 0.2, 0.5, 1, 2, 3, 5, and 7 C, respectively. Moreover, the 2 wt.% V$_2$O$_5$-modified LiNi$_{0.5}$Mn$_{1.5}$O$_4$ provides an enhanced discharge capacity of 116.2 mAh g$^{-1}$ after 200 cycles at 1 C, having a capacity retention of 91.6%, high than that of pure LNMO with a discharge capacity of 103.0 mAh g$^{-1}$ and capacity retention of 85.3%.

1. Introduction

In recent years, lithium-ion battery (LIB) has been considered as one of the most promising devices to meet energy storage. The energy density of LIB can be enhanced by cathode materials with either large specific capacity or high operation voltage [1-2]. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) is one of the most attractive cathode materials for LIBs due to its inherent three-dimensional structure, higher operating voltage (4.7 V) arising from the presence of Ni$^{2+}$/Ni$^{4+}$, and its larger theoretical capacity (146.7 mAh g$^{-1}$) [3-4].

However, this material has some disadvantages. For example, the electrolyte decomposes under a high charging voltage, resulting in surface side-reactions between the electrode and electrolyte, which can lead to capacity deterioration during the charge/discharge process. To improve the electrochemical performance of LNMO material, extensive approaches have been adopted. Surface modification is an effective method to suppress the side reactions and enhance the electrochemical performance of LNMO. A variety of modification materials, including Al$_2$O$_3$ [5], ZrO$_2$ [6], RuO$_2$ [7], TiO$_2$ [8], ZrF$_4$ [9], YPO$_4$ [10], and Li$_2$SnO$_3$ [11] and so on, have been used to modify the surface of LNMO particles. These modification materials can prevent LNMO particles from direct contact with electrolytes. Among the coating materials, V$_2$O$_5$ can be used to modify LNMO due to its relatively higher ionic conductivity and Li$^+$ diffusion coefficient [12]. It has been used to modify other cathode materials, which have obtained enhanced electrochemical performances [13, 14]. In this study, the V$_2$O$_5$-modified LNMO has been prepared, and the structural properties and electrochemical performances of the as-synthesized samples have been studied.
2. Material and Methods

2.1 Synthesis and characterization
Li$_2$CO$_3$, MnO$_2$, and NiO purchased from aladdin were used as raw materials to synthesize the pure LNMO via a solid-state method. First, Li$_2$CO$_3$, NiO, and MnO$_2$ with a stoichiometric ratio of 0.52:0.5:1.5 were mixed in ethanol before being ground at 200 rpm for 9 h using a ball mill. A dry precursor was then formed by drying the mixture at 105 °C for 4 h. The precursor was then sintered for 3 h at 550°C before being calcining for 9 h at 850 °C in air to obtain the pure LNMO.

The 2 wt.% V$_2$O$_5$-modified LNMO sample was synthesized according to the previous procedure [15]. In brief, a stoichiometric amount of vanadiumoxy acetylacetonate (C$_{10}$H$_{14}$O$_5$V) was dissolved in 60 ml ethanol at 80 °C under stirring. Then 2 g of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ was added to the above solution under continuous stirring until the solvent was fully evaporated. Afterwards, the solid mixture was ground and calcined at 400 °C for 3 h in air with a heating rate of 5 °C min$^{-1}$.

X-ray diffraction (XRD, Ultima IV, Rigaku) incorporating Cu Kα radiation was used to characterize the phase structures of all samples. The diffraction patterns were collected at room temperature by scanning stepwise between 20 values of 10 to 90° at 0.02° per 10s. Scanning electron microscopy (SEM, SU 8020, Hitachi) was used to observe microstructures and morphologies of the prepared samples.

2.2 Electrochemical measurements
CR-2032 half-cells were assembled to evaluate the electrochemical performance using galvanostatic charge-discharge tests. Electrodes were fabricated by combining LNMO materials, Super-P and polyvinylidene fluoride in N-methyl-2-pyrrolidone with a mass ratio of 8.5:1:0.5 to form a proportioned slurry. The slurry was then spread on Al foil and dried in a vacuum oven at 105 °C for 12 h. The obtained homogeneous slurries were smeared on aluminum foil and dried at 90°C in a conventional oven to remove the solvent. The electrodes were punched into round disks with diameters of 10 mm and then dried at 105 °C for 24 h in a vacuum oven to eliminate moisture. An Ar-filled glovebox was then used to assemble the half-cells. The electrolyte was 1 M LiPF$_6$ dissolved in a 1:1:1 (volume ratio) mixture of ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate. Metal lithium was used as the counter electrode and Celgard 2400 porous polypropylene was used as the separator. The rate and cycling performance tests were conducted on an automatic galvanostatic charge-discharge unit (Land 2001A, Wuhan, China) with a voltage window of 3.5–5.0 V (The current density of 1 C is 140 mA g$^{-1}$) between 0.2 and 7 C at 25 °C.

3. Result and Discussion

3.1 Material characterization
XRD patterns for pure LNMO and 2 wt.% V$_2$O$_5$-modified LNMO samples exhibit sharp diffraction peaks, as shown in Fig.1, which displays that the two samples are good crystallinity and indexed to the spinel structure (JPCS card No.80-2162). The V$_2$O$_5$ modification did not destroy the crystal structure of the 2 wt.% V$_2$O$_5$-modified LNMO samples. However, no V$_2$O$_5$ diffraction peaks were detected in 2 wt.% V$_2$O$_5$-modified LNMO sample, which may be because of its amorphous form.

Fig. 2a-b show the SEM images of pure LNMO and 2 wt.% V$_2$O$_5$-modified LNMO samples. It can be seen that the as-prepared samples display well-crystallized octahedral morphology. The pure LNMO particles deliver smooth-surfaced. However, some amorphous V$_2$O$_5$ particles were formed on the surface of the 2 wt.% V$_2$O$_5$-modified LNMO sample. The V$_2$O$_5$ coating can protect the LNMO particles from the electrolyte corrosion. Furthermore, the V$_2$O$_5$ modification did not change the particle size of 2 wt.% V$_2$O$_5$-modified LNMO sample compared to pure LNMO.
Fig. 1 XRD patterns of pure LNMO and 2 wt.% V$_2$O$_5$-modified LNMO samples

Fig. 2 SEM images of (a) pure LNMO, (b) 2 wt.% V$_2$O$_5$-modified LNMO

3.2 Electrochemical properties

The rate capabilities for pure LNMO and 2 wt.% V$_2$O$_5$-modified LNMO samples at C-rates from 0.2 to 7 C are shown in Fig. 3a-b. The 2 wt.% V$_2$O$_5$-modified LNMO sample deliver a higher discharge capacity compared to pure LNMO, whose discharge capacities at the high-rate of 5 C and 7 C were 91.2 and 63.9 mAh g$^{-1}$, respectively. While the discharge capacities for 2 wt.% V$_2$O$_5$-modified LNMO are 103.2 mAh g$^{-1}$ and 79.0 mAh g$^{-1}$. The galvanostatic charge–discharge curves of the two samples are shown in Fig. 3c–d. The two samples show similar charge/discharge profiles and exhibit three plateaus at 0.2 and 0.5 C, in accordance with the redox reactions of Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$ at 4.6–4.8 V and Mn$^{3+}$/Mn$^{4+}$ with a short slope at ~4.0 V. The 2 wt.% V$_2$O$_5$-modified LNMO shows a smaller potential difference between the charge and discharge platforms at high C-rates, which demonstrates that the V$_2$O$_5$ coating on the LNMO particles can reduce electrode polarization.

Fig. 4 shows the cycling performances of the two samples at 1 C. The capacity retentions of pure LNMO and 2 wt.% V$_2$O$_5$-modified LNMO samples are 85.3% and 91.9%, respectively, after 200 cycles at 25 °C. The 2 wt.% V$_2$O$_5$-modified LNMO exhibits a better cycling stability compared to pure LNMO, which indicates that the V$_2$O$_5$ modification can improve the cycling stability.
Fig. 3 (a, b) Rate capacities of the two samples from 0.2 C to 7 C; (c, d) the galvanostatic charge/discharge curves at different C-rates for the two samples at 3.5–5.0 V

Fig. 4 Cycling performance of pure LNMO and 2 wt.% V2O5-modified LNMO samples

4. Conclusion
In this study, the 2 wt.% V2O5-modified LNMO material has been prepared by a sol-gel process. After the modification process, an amorphous V2O5 coating layer formed on the surface of LNMO particles. The 2 wt.% V2O5-modified LNMO sample exhibits a better rate capability and cycling stability than that of pure LNMO. These results demonstrate that the V2O5 modification can enhance the electrochemical properties of LNMO cathode material. Therefore, our study provides a facile approach for preparing the 2 wt.% V2O5-modified LNMO sample, which is easily scalable for industrialization for lithium-ion batteries.

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