

Improved electrochemical performance of 5 V spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by La_2O_3 surface coating for Li-ion batteries

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Abstract. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ coated with 1.5 wt.% La_2O_3 was prepared and investigated as cathode materials for lithium ion batteries. The samples was characterized by XRD, SEM and EDX. After the 1.5 wt.% La_2O_3 coating, the lattice structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is not destroyed and a La_2O_3 coating layer has formed on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles. The 1.5 wt.% La_2O_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibits a higher rate capacity, with discharge capacity between 3.5 and 5 V of 131.9, 127.1, 126.5, 120.7, 114.1 and 101.5 mAh g^{-1} at rates of 0.2, 0.5, 1, 2, 3 and 5 C (1 C = 140 mAh g^{-1}), respectively. The results indicate that the La_2O_3 coating could reduce the electrode polarization and enhance the rate capacities.

1 Introduction

High voltage cathode materials are playing an important role in the development of high energy and power lithium-ion batteries for their potential applications in hybrid electric vehicles and renewable energy storage devices [1-4]. Spine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) is considered as one of the most attractive cathode materials due to its high operating voltage (at about 4.7V vs Li^+) and high specific energy of 658 Wh kg^{-1} , which is much higher than commercial cathode materials such as LiCoO_2 (518 Wh kg^{-1}), LiMn_2O_4 (400 Wh kg^{-1}), LiFePO_4 (495 Wh kg^{-1}), and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (576 Wh kg^{-1}). However, the LNMO acts as cathode material may exist two problem. On the one hand, the Mn dissolution into the electrolyte could result in the structure collapse and capacity degradation. On the other hand, the decomposition of the electrolyte would generate HF, which would also corrode the LNMO material, leading to the capacity fading.

Recently, many efforts have been devoted to resolve the above-mentioned problem. Surface coating is an effective method to improve the electrochemical performance of LNMO material. These surface coating materials include metals (Zn [5]), oxides (ZnO [6], Al_2O_3 [7-8], SiO_2 [9], Bi_2O_3 [10], ZrO_2 [11], MgO [12], Fe_2O_3 [13-14], LiSiO_3 [15], LiNbO_3 [16], RuO_2 [17], CeO_2 [18], TiO_2 [19], CoAl_2O_4 [20]), phosphates (Li_3PO_4 [21], FePO_4 [22]), fluorides (AlF_3 [23]), GaF_3 [24]) and some conductive components (carbon nanotubes [25], or graphene [26]). La_2O_3 with excellent thermal stability has been used to coat the LiCoO_2 and improve the electrochemical performances [27]. In our previous work, we use the La_2O_3 to modify the LTO to suppress the electrolyte decomposition and enhance the rate capacity of LTO anode material [28]. Inspired by these results,

we propose to use the La_2O_3 as a coating layer to determine whether it is effective to improve the electrochemical performance of LNMO.

In this paper, 1.5 wt.% La_2O_3 was successfully coated on the surface of LNMO. The structure and electrochemical performance of the La_2O_3 coated LNMO sample was investigated and reported below.

2 Material and methods

2.1 Synthesis and characterization

Pure LNMO powders were synthesized by a solid-state ball-milling and spray drying method. Specifically, a stoichiometric amount of NiO , Li_2CO_3 , MnO_2 and deionized water were mixed by ball milling at 300 rpm for 10 h using zirconia as the milling media, The mixture was subsequently used the spray drying to get the precursor powders. Finally, the precursor powders were calcined at 500°C for 5h and 800°C for 8 h in an air atmosphere to obtain pure LNMO. The molar ratio of $\text{Li}:\text{Ni}:\text{Mn}$ was 1:0.5:1.5 and excessive Li (5%) was added to compensate for the volatilization of Li during the calcined process.

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aladdin) and polyvinyl alcohol (PVA, degree of polymerization is 1500) were purchased for this work. The La_2O_3 -coated LNMO sample was achieved by the following steps: LNMO (5 g) was dispersed in deionized water, then the mixture stirred for 2 hours. The calculated 1.5 wt.% of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to form La_2O_3 and 1.5 wt.% polyvinyl alcohol were dissolved in warm deionized water and added dropwise to the dispersed LNMO. The mixture was continuously stirred for 1 hours at 25 °C and continuously stirred at 100 °C to evaporate the water, then the mixed solid

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powder was calcined at 500 °C for 5 hours in air to obtain the 1.5 wt.% La₂O₃-coated LNMO sample.

Powder X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu K_α radiation was used to characterize the phase composition and crystal structures of all the samples. The diffraction patterns were collected at room temperature by step scanning in the range of 10–90° at a scanning rate of 0.02° per 10 s. The morphology of the materials was characterized by SEM (Hitachi SU8020, Japan). The microstructure and EDX mapping of all samples were also observed by SEM (INCA Penta-FETx3).

2.2 Electrochemical measurements

The electrochemical properties of all samples were tested by adopting a CR2032 coin-type half-cell with Li foil as the counter electrode. The cathode slurry was prepared by homogeneously mixing the active materials, Super-P, and polyvinylidene fluoride (PVDF) in a mass ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP) solvent. Then, the slurry was cast onto a Al foil and dried for 12 h in vacuum at 105°C. Finally, the electrode laminate was punched into disks (10 mm in diameter) and dried in a vacuum oven at 105°C for 24 h. The coin cell was assembled entirely in an argon-filled glovebox. The separator was Celgard 2400 (Celgard Inc., USA), and the electrolyte (Capchem Technology (Shenzhen) Co., Ltd.) was a solution of 1 mol L⁻¹ LiPF₆ in ethylene carbonate, ethyl methyl carbonate, and diethyl carbonate (1:1:1, volume ratio).

The galvanostatic charge-discharge tests were conducted on an automatic galvanostatic charge-discharge unit (Land 2001A, Wuhan, China) between 3.5 and 5 V and at charge/discharge C-rates between 0.2 and 5 C (1 C = 140 mAh g⁻¹) at 25°C.

3 Result and discussion

3.1 Material characterization

The XRD patterns of pure LNMO and the La₂O₃-coated LNMO are presented in Fig. 1. All the XRD patterns are indexed to the standard spinel structure of LNMO (card NO. 80-2162) with *Fd-3m* space group. The structure of LNMO was not destroyed by La₂O₃ coating. There is a small peak (marked with '*'), which is corresponding to an impurity phase of Li_xNi_{1-x}O₂, demonstrating an oxygen loss reaction at high temperatures during the calcining process. Furthermore, there were no peaks that indicate the existence of La₂O₃. This may be attribute to the low La₂O₃ content or its amorphous state.

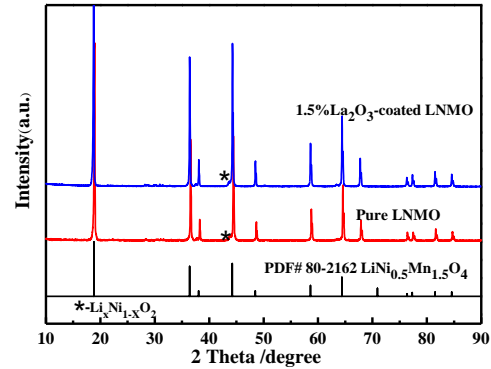
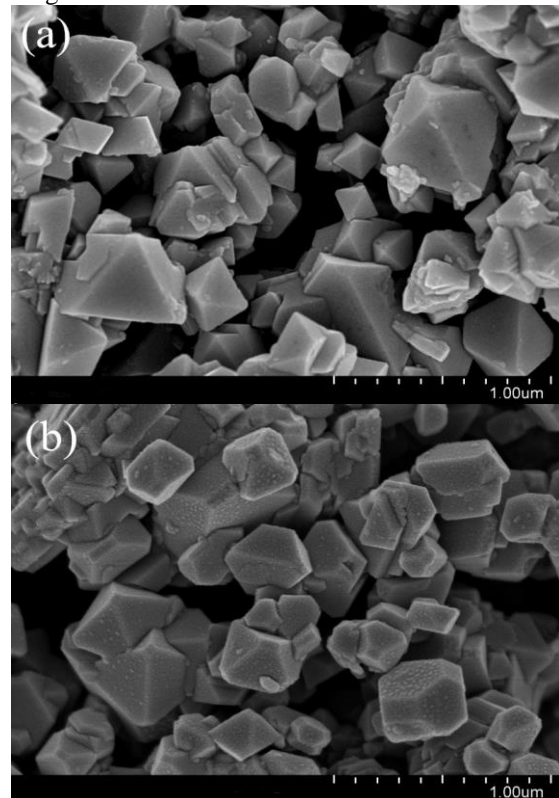


Figure1: XRD patterns of pure LNMO, 1.5 wt.% La₂O₃-coated LNMO and the standard XRD patterns of LNMO

The morphologies of pure LNMO and the 1.5 wt.% La₂O₃-coated LNMO are characterized by SEM observations as shown in Fig. 2. It can be observed that pure LNMO has a smooth surface as clearly shown in Figure 2a. In contrast, the SEM image of the 1.5 wt.% La₂O₃-coated LNMO shows a rough surface and a number of tiny particles over LNMO as shown in Figure 2a. The tiny particles may be the La₂O₃ coating layer. The EDX mapping images of the 1.5 wt.% La₂O₃-coated LNMO are shown in Fig. 2c. The presence of La, Ni, Mn and O can be found, which shows a homogeneous distribution of La, element on the surface of LNMO after coating.



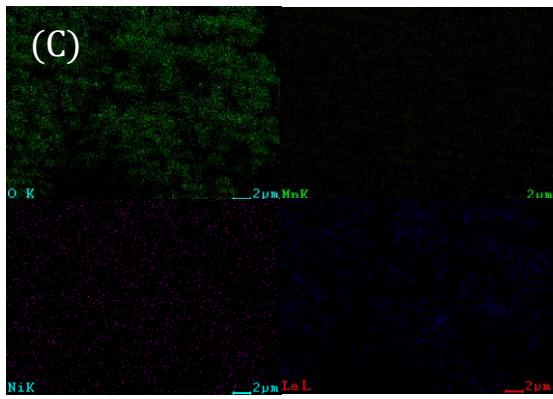


Figure 2: SEM images of (a) pure LNMO and (b) 1.5 wt.% La₂O₃-coated LNMO. (c) EDX mapping of 1.5 wt.% La₂O₃-coated LNMO

3.2 Electrochemical properties

Fig. 3a-b compares the rate capabilities of pure LNMO and the 1.5 wt.% La₂O₃-coated LNMO at C-rates from 0.2–5 C between 3.5 and 5V. It is worth noting that the 1.5 wt.% La₂O₃-coated LNMO exhibits a higher rate capacity. The discharge capacity values of the 1.5 wt.% La₂O₃-coated LNMO are 131.9, 127.1, 126.5, 120.7, 114.1 and 101.5 mAh g⁻¹ at rates of 0.2, 0.5, 1, 2, 3 and 5 C mAh g⁻¹ (1 C = 140 mAh g⁻¹), respectively, which is higher than that of pure LNMO with the discharge capacity values are 130.4, 121.7, 112.4, 103.3, 95.2 and 64.7 mAh g⁻¹, respectively. The galvanostatic charge-discharge curves of pure LNMO and the 1.5 wt.% La₂O₃-coated LNMO are shown in Fig. 3c–d. It can be observed that the two samples have similar charge/discharge profiles, demonstrating that there are two discharge plateaus in the potential region of 4.7 V and one lower plateau at around 4.0 V. The 1.5 wt.% La₂O₃-coated LNMO displays a smaller potential difference between the charge and discharge platforms, especially at high C-rates. This phenomenon indicates that the La₂O₃-coating can reduce electrode polarization and suppress the side reactions between LNMO and the electrolytes and enhance the rate capacities.

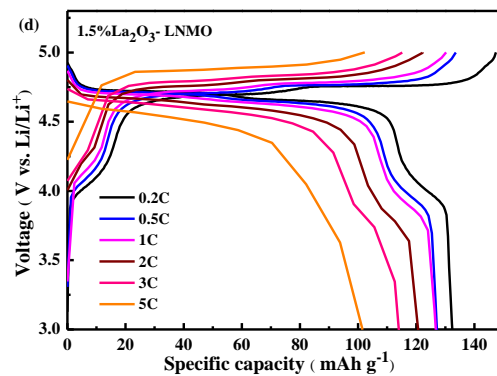
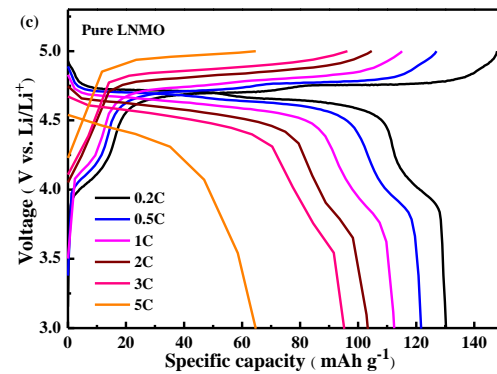
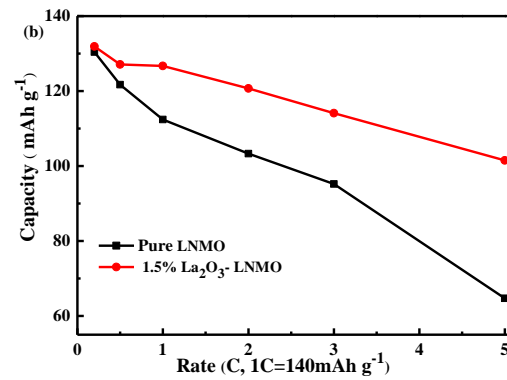
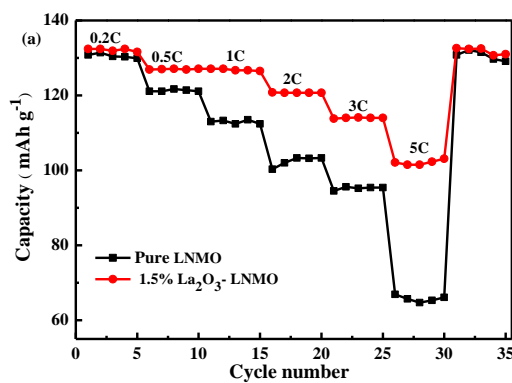


Figure 3: (a) Rate capacity of pure LNMO and 1.5 wt.% La₂O₃-coated LNMO from 0.2C to 5C, (b) discharge capacity as a function of the C-rates for pure LNMO and 1.5 wt.% La₂O₃-coated LNMO and (c-d) galvanostatic charge-discharge curves at different C-rates for pure LNMO and 1.5 wt.% La₂O₃-coated LNMO between 3.5 and 5 V (1C = 140 mAh g⁻¹)

4 Conclusion

In summary, the 1.5 wt.% La₂O₃ has been successfully coated on the surface of LNMO. The characterization results show that the La₂O₃ coating does not destroy the formation of LNMO and a La₂O₃ coating layer distributes uniformly on the surface of LNMO particles. The electrochemical results indicate that the 1.5 wt.% La₂O₃-coated LNMO exhibits a higher rate capability over pure LNMO. This is attributed to the fact that the La₂O₃ coating layer could protect the transition metal ions from dissolving into the electrolyte and minimizing harmful side reactions between the LNMO and electrolyte. Therefore, Our studies display that the La₂O₃ coating offers an important benefit to increase the rate

capacity of LNMO cathode material for lithium ion batteries.

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