Effects of LiAlO$_2$ coating on electrochemical performance of single-crystal LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$

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Abstract: The LiAlO$_2$-coated commercial single-crystal LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ were synthesized by a solid-state method. The structure and electrochemical performance of the prepared materials were investigated by X-ray diffraction, scanning electron microscopy and galvanostatic charge-discharge tests. After LiAlO$_2$ coating, single-crystal LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ retains a well-developed layered structure and exhibits higher discharge capacities. The LiAlO$_2$-coated LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ sample delivers higher discharge capacities of 185.1, 176.3, 167.3, 156.9, and 138.9 mAh g$^{-1}$ at rates of 0.2C, 0.5C, 1C, 2C, and 5C, respectively. The results indicate that the LiAlO$_2$ coating could reduce the electrode polarization and enhance the rate capacities.

1. Introduction

Lithium ion batteries are increasingly widely used as power sources in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1-2]. Among the various cathode materials, LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ exhibits more advantages for EVs and HEVs owing to its low cost, high capacity, improved cycling stability, and enhanced safety performance [3-4]. LiNi$_{x}$Co$_{y}$Mn$_{2-x-y}$O$_2$ (NCM), one of the LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ materials system, displays good electrochemical performance than both LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ and LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$. However, LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ exhibits some inherent shortages, such as the poor rate capability and insufficient capacity retention, especially at high cutoff voltages [5]. To resolve the above problems, various techniques have been adopted to enhance the electrochemical performance of NCM. Surface modification is one of effective methods to improve the properties of NCM material. The surface of NCM cathode materials have been coated with inorganic materials such as metal oxides (Al$_2$O$_3$, SiO$_2$, ZrO$_2$, TiO$_2$, Co$_3$O$_4$, MnO$_2$, ZnO, CeO$_2$, and Li$_2$ZrO$_3$), fluorides (AlF$_3$), and phosphates (AlPO$_4$, and Mn$_3$(PO$_4$)$_2$). Moreover, LiAlO$_2$, as a well-known lithium-ion conductor, has been utilized to coat onto LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ materials exhibiting an enhanced electrochemical performance than pristine one [6].

In this paper, 2 wt.% LiAlO$_2$ was firstly successfully coated on the surface of single-crystal LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$. The structure and electrochemical performance of the LiAlO$_2$ coated NCM were investigated and discussed.

2. Material and methods

2.1. Synthesis and characterization

The LiAlO$_2$-coated commercial single-crystal LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ were synthesized by a solid-state method. LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (10 g) and stoichiometric LiOH·H$_2$O were dispersed in alcohol, magnetic stirring for 1 hours at 40 °C. Then, stoichiometric Al(OH)$_3$ was added to the dispersed the mixture under...
continuous magnetic stirring for 1 hours at 40 °C. The mixture was stirred at 90 °C to evaporate the alcohol, then the mixed solid powder was calcined at 600 °C for 4 hours in air to obtain the 2 wt.% LiAlO2-coated NCM (LAO@NCM) sample.

Powder X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu Kα 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).

2.2. Electrochemical measurements
The electrochemical performances 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 Al foil and dried for 12 h in vacuum at 105°C. Finally, the electrode laminate was punched into disks (12 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).

Galvanostatic charge-discharge tests were carried out under different C-rates of 0.2C, 0.5C, 1C, 2C, and 5C (the current density is 180mA g−1 at the 1C rate) over a voltage range of 2.6–4.5 V using an automatic galvanostatic charge-discharge unit (Land 2001A, Wuhan, China).

3. Result and discussion

3.1. Material characterization
Fig.1 presents the XRD patterns of pure NCM and LAO@NCM. All of the XRD diffraction peaks are indexed to the hexagonal α-NaFeO2 structure (space group R-3m). As shown in Fig.1, the LiAlO2-coated NCM exhibits no new peaks or impurities compared to the pristine NCM, which may due to the amorphous structure of the LiAlO2 coating. The distinct splitting of the (006)/(102) and (108)/(110) peaks of both samples demonstrates that pure NCM and LAO@NCM have a well-developed layered structure [7], which indicates that LiAlO2 coating does not change the structure of single-crystal NCM.

![XRD patterns of pure NCM and LAO@NCM](image)

Fig.1. XRD patterns of pure NCM and LAO@NCM
The morphology of pure NCM and LAO@NCM was examined by SEM as shown in Figure 2. The pure NCM exhibited a well-crystallized structure and clean surface in Figure 2 (a). Contrary to the pure NCM, the LAO@NCM sample had a rough morphology with tiny particles on the surface, which may be the formed LiAlO2 coating layer.

![SEM images of NCM and LAO@NCM](image)
3.2. Electrochemical properties

The rated capacities and galvanostatic charge-discharge curves of two samples in the voltage range of 2.6-4.5 V at different C-rates are presented in Figure 3. As shown in the Figure 3 (a), LAO@NCM sample exhibits better capacities than pure NCM at different rates. The LAO@NCM sample delivers higher discharge capacities of 185.1, 176.3, 167.3, 156.9, and 138.9 mAh g⁻¹ at rates of 0.2C, 0.5C, 1C, 2C, and 5C, respectively. The initial discharge capacity is 175.4 mAh g⁻¹ of LAO@NCM higher than 174 mAh g⁻¹ of pure NCM, and the initial coulombic efficiency is 82.9% and 83.4% of LAO@NCM and pure NCM, respectively. The rate performance result shows that the LAO coating layer is beneficial to improve the rate capability of single-crystal LiNi₀.₆Co₀.₂Mn₀.₂O₂.

Figure 3 (b) and (c) show the galvanostatic charge-discharge curves of LAO@NCM and pure NCM at 0.2 and 0.5 C-rates. It is clear that LAO@NCM sample has a longer voltage plateaus than pure NCM at 0.2C and 0.5C, which indicates that LAO@NCM sample has higher charge-discharge capacity and smaller differentials (ΔV between the charge and discharge voltage plateau), implying a lower electrode polarization of NCM after LiAlO₂ coating.
Fig. 3. (a) Discharge capacity at different C-rates and (b-c) galvanostatic charge-discharge curves at 0.2C and 5C in the range of 2.6–4.5 V.

4. Conclusion
In this work, LiAlO₂-coated commercial single-crystal NCM was synthesized successfully by a solid-state reaction. The characterization results show that the LiAlO₂ coating does not destroy the structure of NCM and a LiAlO₂ coating layer distributes uniformly on the surface of NCM particles. The electrochemical results indicate that the LiAlO₂-coated NCM exhibits a higher rate capability than pure NCM. Therefore, we found an effective coating technique to enhance the electrochemical performance of NCM material.

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