

Full paper

Significantly improving cycling performance of cathodes in lithium ion batteries: The effect of Al₂O₃ and LiAlO₂ coatings on LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂

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ABSTRACT

LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (NCM) is a highly potential cathode material for lithium-ion batteries (LIBs). However, its poor rate capability and cycling performance at high cutoff voltages have seriously hindered further commercialization. In this study, we successfully design an ultra-thin lithium aluminum oxide (LiAlO₂) coating on NCM for LIBs. Compared to Al₂O₃, the utilization of lithium-ion conducting LiAlO₂ significantly improves the NCM performance at high cutoff voltages of 4.5/4.7 V. The study reveals that the LiAlO₂-coated NCM can maintain a reversible capacity of more than 149 mA h g⁻¹ after 350 cycles with 0.078% decay per cycle. Furthermore, LiAlO₂-coated NCM exhibits higher rate capacities [206.8 mA h g⁻¹ at 0.2 C (50 mA g⁻¹) and 142 mA h g⁻¹ at 3 C] than the Al₂O₃-coated NCM (196.9 mA h g⁻¹ at 0.2 C and 131.9 mA h g⁻¹ at 3 C). Our study demonstrates that the ultra-thin LiAlO₂ coating is superior to Al₂O₃ and significantly improves the capacity retention and rate capability of NCM for LIBs.

1. Introduction

The increasing demand for high energy and power density lithium-ion batteries (LIBs) has stimulated great research interest in high performance cathode materials for application in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1–7]. Among the various cathode candidates, LiNi_{1-x-y}Co_xMn_yO₂ materials have displayed several advantages including low cost, high capacity, improved cycling stability, and enhanced safety performance [8–10]. Within this system, nickel-rich layered LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (NCM) displays good Li-ion diffusivity with minimal temperature dependence [11], as well as a higher specific capacity than both LiNi_{0.3}Co_{0.3}Mn_{0.3}O₂ and LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂. As a result, NCM has been recognized as one of the most promising cathode materials for application in high performance LIBs [11,12]. However, NCM exhibits several limitations, including poor rate capability and insufficient capacity retention, especially at high cutoff voltages [13]. These challenges are a result of: (i) structural instability originating from the surface sites and distortion of the rhombohedral phase due to the migration of transition metal ions into Li⁺ vacant sites, leading to the formation of spinel-like structures and electrochemically inert NiO-

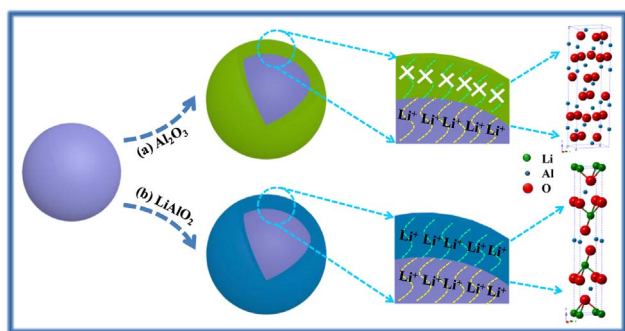
like phases [13–15]; (ii) dissolution of metal ions in LiPF₆-based electrolytes due to HF corrosion [16,17]; and (iii) electrolyte decomposition at the cathode and subsequent formation of a solid electrolyte interphase (SEI) layer, resulting in increased surface impedance [18]. These challenges greatly hinder practical application in LIBs [17].

To address these challenges, various techniques such as surface modification [19], elemental doping [20], and concentration gradient structures [21] have been utilized to enhance the electrochemical performance of NCM cathode materials. Previously, surface modification has been shown to significantly improve the performance of electrode materials [16,22]. Inorganic compounds such as metal oxides (SiO₂ [23], Co₃O₄ [24], MoO₃ [25], ZrO₂ [26], ZnO [27], CeO₂ [28], and Al₂O₃ [26,29,30]), fluorides (AlF₃ [31]), and phosphates (Mn₃(PO₄)₂ [32]) have been coated onto LiNi_{1-x-y}Co_xMn_yO₂ to improve the structural stability between the active materials and electrolytes. For example, Co₃O₄-coated LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ was reported to deliver a capacity ranging from 186.5 mA h g⁻¹ to 114.1 mA h g⁻¹ in the first 100 cycles [24], and the Al₂O₃-coated LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ revealed higher capacity retention of 85% after 100 cycles, in comparison to the pristine electrode (only 75%) [29]. Among these compounds, metal

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Scheme 1. The difference of two coatings on NCM: (a) metal oxide and (b) solid state electrolyte.

oxides, especially Al_2O_3 , effectively prevent the electrode surface from contacting the organic electrolyte, thus alleviating electrolyte decomposition [29]. However, an Al_2O_3 coating may also suppress lithium-ion transfer at the electrode interface, thereby limiting battery performance [17,33]. In contrast, LiAlO_2 coatings are well known as lithium-ion conductors [33–35] and have greater lithium diffusivity than Al_2O_3 [33,36]. It has attracted great attention, such as LiAlO_2 -inlaid $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ exhibiting a better electrochemical performance than the pristine one [37]. These properties enable LiAlO_2 to overcome the limited lithium-ion conductivity of metal oxide coatings (Scheme 1) and increase $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ performance in LIBs. To the best of our knowledge, few reports focus on the effect of LiAlO_2 coatings on $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode materials at high cutoff voltages of 4.5/4.7 V.

In this study, both Al_2O_3 and LiAlO_2 coatings were successfully designed on NCM cathodes for LIBs. Notably, the significant effects of the two coatings on the structural and electrochemical performance of NCM were addressed at high cutoff voltages of 4.5/4.7 V. The resulting structures and electrochemical behavior were discussed in detail.

2. Experimental

2.1. Material synthesis

Commercial NCM was utilized as the cathode material to study the effects of Al_2O_3 and LiAlO_2 coatings on battery performance. Both coatings were synthesized via a sol-gel process. LiAlO_2 -coated NCM was produced by mixing NCM, aluminum(III) sec-butoxide [$\text{Al}(\text{sec-OC}_4\text{H}_9)_3$, 97%, Aladdin], ethyl acetoacetate (EAcAc), ultrapure water, and ethanol. Lithium methoxide (LiOMe , 98%, Aladdin) was added to the mixture, and stirred continuously at room temperature. The afforded mixture was transferred into a Teflon-lined autoclave and maintained at 150 °C for 15 h. The product was washed with ethanol and

subsequently dried in an oven at 80 °C for 4 h. The blend was then collected and calcined. Concentrations of 0.125, 0.25, 0.60, 1.25, 2.5, and 12.5 mol% of LiAlO_2 -coated NCM were synthesized using this method. These were labelled as Li-Al-O-1, Li-Al-O-2, Li-Al-O-3, Li-Al-O-4, Li-Al-O-5, and Li-Al-O-6, respectively. Similar concentrations of Al_2O_3 -coated NCM were synthesized using the above method without the addition of LiOMe and labelled as Al-O-1, Al-O-2, Al-O-3, Al-O-4, Al-O-5, and Al-O-6, respectively.

2.2. Material characterization

The phase of each sample was identified by X-ray diffraction (XRD, Bruker AXS D8Advance). Particle size distribution was estimated from low-angle laser light scattering (LALLS) measurements (Malvern Mastersizer 3000). The sample morphologies and microstructures were analyzed by scanning electron microscopy (SEM, Hitach SU8010) and transmission electron microscopy (TEM, JEOL JEM-3000F). Moreover, energy dispersive X-ray spectroscopy (EDS) mapping was carried out using OXFORD 7426 as the SEM attachment, with an acceleration voltage of 20 kV. Elemental composition information was elucidated using X-ray photo-electron spectroscopy (XPS, VG ESCALAB MK II).

2.3. Electrochemical measurements

CR2032 coin cells were utilized to study the electrochemical performance of the cathode materials. The cathode electrode comprised 80 wt% active material, 10 wt% acetylene black and 10 wt% PVDF binder. Lithium metal foil was used as anode. LiPF_6 (1 M) in a 1:1:1 (v/v/v) dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC)/ethylene carbonate (EC) was used as electrolyte. Cell assembly was carried out in a dry argon-filled glove box. Electrochemical tests were carried out using an automatic galvanostatic charge/discharge unit (LAND CT2001A battery tester) between 2.7 and 4.5/4.7 V (versus Li/Li^+) at room temperature. Cyclic voltammetry (CV) tests were performed on a Princeton Applied Research VersaSTAT 4 electrochemical workstation at a scan rate of 0.1 mV s^{-1} and a potential range of 2.7–4.5 V (vs. Li/Li^+). Electrochemical impedance spectroscopy (EIS) was conducted on a Princeton Applied Research VersaSTAT 4 electrochemical workstation, using 2-electrode cells (amplitude voltage is 5.0 mV, and frequency range, 10 mHz–100 kHz).

3. Results and discussion

As shown in Fig. 1(i), the NCM XRD diffraction peaks exhibit sharp and well defined Bragg lines corresponding to a hexagonal $\alpha\text{-NaFeO}_2$ structure (space group $R\text{-}3m$). The XRD patterns of Al-O-1, Li-Al-O-1, Al-O-4, Li-Al-O-4, Al-O-6 and Li-Al-O-6 are compared in Fig. 1(ii)–(vii). All diffraction peaks in the XRD patterns are indexed on the basis of a

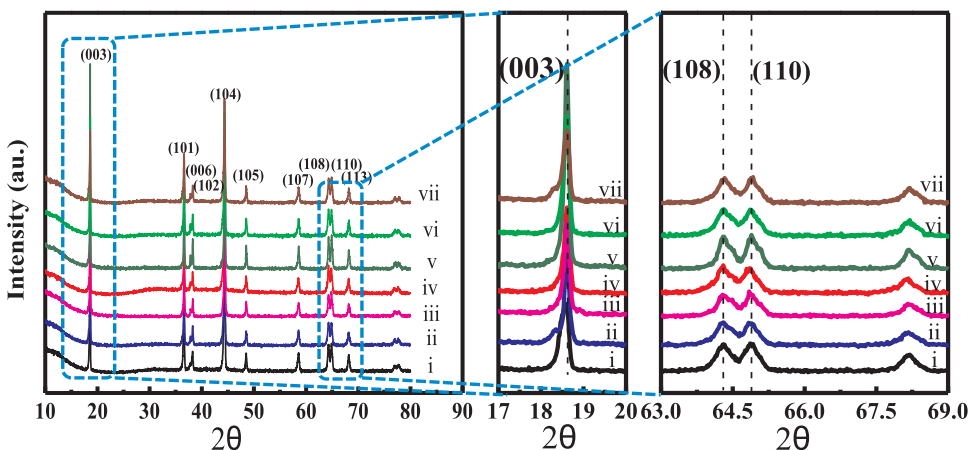


Fig. 1. XRD patterns of (i) NCM, (ii) Al-O-1, (iii) Li-Al-O-1, (iv) Al-O-4, (v) Li-Al-O-4, (vi) Al-O-6 and (vii) Li-Al-O-6.

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