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Highly crystalline alumina surface coating from hydrolysis of aluminum isopropoxide on lithium-rich layered oxide

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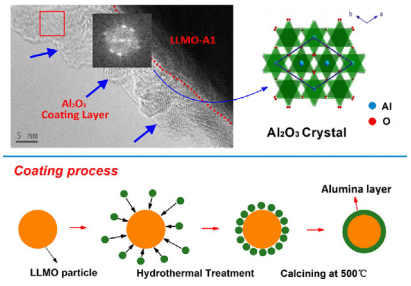
HIGHLIGHTS

- The $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ has been synthesized via sol–gel method.
- Highly crystalline Al_2O_3 crystals coating layer is covered on the surface of $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ particles.
- The bare cathode material delivers a high discharge capacity of 268.2 mAh g^{-1} at 0.1C between 2.0 V and 4.8 V.
- The highly crystalline Al_2O_3 coated material has 98% capacity retention after 100 cycles at 1C.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-rich layered oxides, $xLi_2MnO_3 \cdot (1-x)LiMO_2$(M = Ni, Mn, Co), have been under intense investigation as high-performance cathode materials for lithium ion batteries due to their high discharge capacity, low cost and environmental benignity. Unfortunately, the commercialized application of these cathode materials have so far been hindered by their severe capacity and voltage fading during high voltage cycling (>4.5 V *vs.* Li/Li^+). In an attempt to overcome these problems, herein, highly crystalline Al_2O_3 layer from the hydrolysis of aluminum isopropoxide are coated on $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ with controlling the growth of Al_2O_3 crystals. The coin cell with bare cathode material delivers a high discharge capacity over 268.2 mAh g^{-1} between 2.0 V and 4.8 V, while the Al_2O_3 coated cathode material shows the excellent cycling stability corresponding to 98% capacity retention after 100 cycles at 1C. More importantly, the highly crystalline Al_2O_3 coated cathode materials exhibit a significantly lower discharge voltage decay compared to the bare cathode materials, which could be ascribed to the suppression of the layered-to-spinel transformation by compact and highly crystalline Al_2O_3 layer. The results here will shed light on developing cathode materials with special structures and superior electrochemical properties for high-performance lithium ion batteries.

1. Introduction

Advanced lithium-ion batteries (LIBs) with high energy density and long cycle life are essential for automotive applications such as

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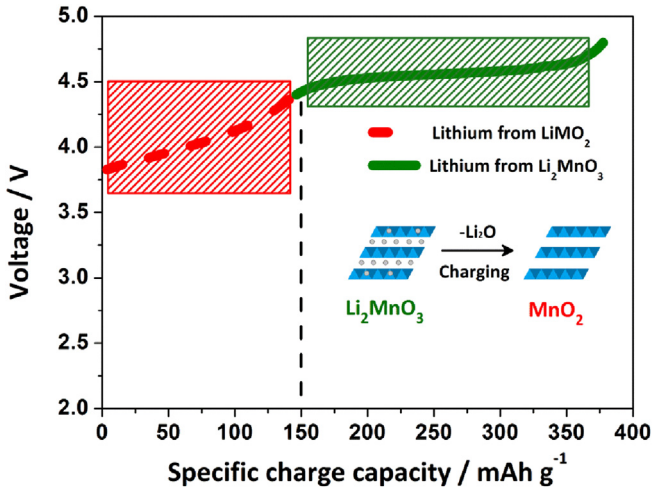

Fig. 1. First charge curves of lithium-rich layered oxide at 2.0–4.8 V. The regions marked red dashed line and blue solid line refer, respectively, to the sloping and plateau regions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

plug-in hybride electric vehicles (PHEVs) or electric vehicles (EVs) [1–3]. Lithium-rich layered oxide, commonly designated as $xLi_2MnO_3\cdot(1-x)LiMO_2$(M = Ni, Mn, Co), is currently under world-wide development for LIBs. An advantage of these materials is that they display a reversible capacity of 230 mAh g^{-1} or more, [4–9] which is significantly higher than the capacity offered by layered $LiCoO_2$ (~140 $mAhg^{-1}$), spinel $LiMn_2O_4$ (~110 mAh g^{-1}) and olivine $LiFePO_4$ (~150 mAh g^{-1}) cathode materials [10].

The high capacity delievered by $xLi_2MnO_3\cdot(1-x)LiMO_2$ cathode materials has been attributed to the electrochemical activation of a Li_2MnO_3 component within the crystal lattice [7–9,11]. In short, Li^+ ions in $LiMO_2$ is removed from the lithium layers during the initial charging process up to a potential near 4.4 V *vs.* Li/Li^+. Above this potential, the Li_2MnO_3 component is activated, as reflected by a long plateau at about 4.5 V, as seen in Fig. 1 [7,12,13]. However, on a practical note, certain challenges need to be overcome before high-capacity $xLi_2MnO_3\cdot(1-x)LiMO_2$ cathode materials will be widely adopted and commercialized: (1) Manganese dissolution occurs at high electrode potentials, resulting in a cross interaction with the lithiated graphite electrode and its protective solid-electrolyte interphase layer. (2) High-capacity $xLi_2MnO_3\cdot(1-x)LiMO_2$ cathode materials are prone to react with the electrolyte operating at high oxidizing potentials. (3) The average cell voltage decay during the repeated cycling of the lithium-rich layered oxide cathode materials [14–21].

The surface modification technique has been reported as an effective approach to improve the cycling performance of $xLi_2MnO_3\cdot(1-x)LiMO_2$ cathode materials by coating conductive carbon materials, phosphates, amphoteric oxides, and composite oxides [15,22–36]. A recent report noted that enhanced capacity on cycling was achieved upon the well coating of MgO on the surface of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathode material [22,23]. For example, the 2 wt.% MgO coated cathode exhibits the excellent cycling stability with capacity retention of 96.4% after 100th cycle. Other surface coating of electrochemically inactive materials (such as ZrO_2, [24] Li_2TiO_3, [25] ZnO, [27] $AlPO_4$ [28]) on the particle of material is also considered to be an effective way to improve the capacity retention by preventing side reaction between cathode and electrolyte. The surface coating suppresses HF attack by scavenging of HF in the electrolyte through acid base reaction, leading to improved capacity retention. Despite these improvements, Al_2O_3 coating has been experimentally proven to enhance the cycling behavior of spinel $LiMn_2O_4$, $LiCoO_2$ cathodes [29–32] and lithium-rich layered oxides [33–36]. Park et al. [33] have reported Al_2O_3 modified $Li[Li_{0.167}Ni_{0.233}Co_{0.1}Mn_{0.467}Mo_{0.033}]O_2$ cathode material. They explained that Al^{3+} ions incorporate into the transition metal layers and modify the surface structure, thus playing a crucial role in improving safety and stability of lithium rich layered oxides. Other groups, such as Belharouak et al., [35] have tried to utilize the technique of atomic layer deposition (ALD), which can deposit Al_2O_3 layers onto the cathode films at an atomic-scale precision. Indeed, these Al_2O_3 coating layers are amorphous and therefore can be easily damaged by the volume change of cathode materials upon cycling. Xu et al. [31] have reported Al_2O_3 coated $LiMn_2O_4$ cathode material. They explain that when the temperature increases to a higher level (such as 700 and 850 °C), the Al_2O_3 coating exhibits well developed crystallinity. According to their report, the cycle life is as good as expected. However, the common procedure of preparing Al_2O_3 coated cathode material is carried out using $Al(NO_3)_3$

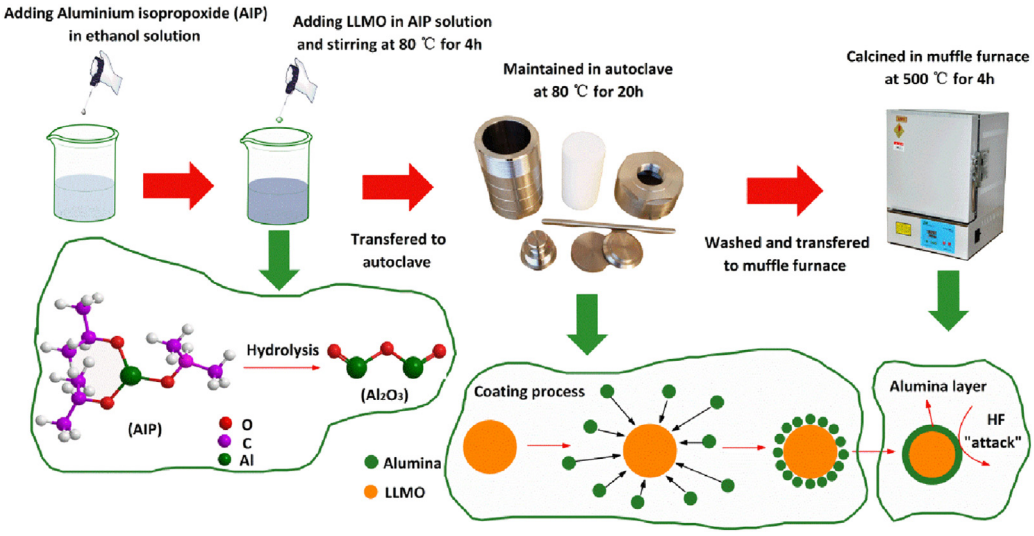

Fig. 2. Illustration of the alumina coating process, including the hydrolysis of aluminum isopropoxide (AIP) and coating process of alumina layer on the surface of lithium-rich layered oxide particle.