Facile synthesis and enhanced electrochemical performances of Li_2TiO_3 -coated lithium-rich layered $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ cathode materials for lithium-ion batteries

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ABSTRACT

Li_2TiO_3 -coated Li-rich layered $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ ($0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$) compound has been successfully synthesized for the first time through a syn-lithiation strategy. In this approach, $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ precursor is first prepared by a co-precipitation method, then it is coated with TiO_2 through a reaction between $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$, and finally $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O} @ \text{TiO}_2$ is simultaneously lithiated to form Li_2TiO_3 -coated Li-rich layered oxide. Both the cyclability and high-rate capability of Li-rich layered cathode materials have been greatly improved by Li_2TiO_3 coating. Meanwhile, the Li_2TiO_3 coating layer also reduces the polarization of the electrode and retards voltage drop during cycling. The reversible capacity of the 3 mol% Li_2TiO_3 -coated Li-rich layered cathode material at the 100th cycle at a large current density of 100 mA/g is significantly enhanced to 105 mAh/g from 78 mAh/g of the un-coated sample. The enhancements of the electrochemical performance can be largely attributed to the stabilization of the interface between the cathode and electrolyte, the three-dimensional path for Li^+ -ion and better conductivity after Li_2TiO_3 coating. It is also disclosed that the amount of Li_2TiO_3 coating also has a large influence on the electrochemical performances and it is necessary to optimize the specific capacity, cycling stability and rate capability through tuning the content of Li_2TiO_3 coating.

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1. Introduction

Lithium-ion batteries (LIBs) are being widely applied in the fields of electronic products such as mobile phones, laptops, cameras and so on. But the energy density of current LIBs is still low and

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not enough for EVs and HEVs [1–8]. The energy density of LIB is mainly restricted by the low capacity of cathode material. The current cathode materials are LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and $\text{LiNi}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333}\text{O}_2$, spinel LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, olive LiFePO_4 , and so on [9–13]. But the rechargeable capacity of these cathode materials is less than 200 mAh/g, which cannot meet the demand for EVs and HEVs. Recently, lithium-rich layered nickel manganese oxides (LLOs, represented by either $\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{(1-x)/3}\text{O}_2$ or $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$, in which M is a transition metal or a mixture of transition metals) have attracted more and more attentions due to their high capacity provided by the extra Li ions [14]. For instance, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ ($x = 0.5, 0.7$) could deliver an anomalously high discharge capacity of more than 286 mAh/g (at a current rate of 0.05 mA/cm² and 50 °C), which is almost twice of LiCoO_2 [15]. Lithium-rich layered oxides materials have been regarded as prospective alternatives for LiCoO_2 toward better Li-ion batteries. However, there are still some challenges for lithium-enriched materials such as its large irreversible capacity during the first cycle and poor rate capability [16,17]. In addition lithium-rich layered cathodes also exhibit a gradual voltage drop during the cycling, which results in the reduction of the energy density. Elements substitution such as Co, Cr, Al, Ti, and so on has been extensively applied to improve the electrochemical performance of lithium-enriched layered cathode material for Li-ion batteries [18,19].

Recently, surface coating of cathode materials with electrochemically inert oxides and phosphates, such as AlF_3 , Al_2O_3 , CeO_2 , ZrO_2 , SiO_2 , ZnO , AlPO_4 and Li-Ni-PO_4 [15,20–22], has become another effective method to improve the electrochemical performance of LIBs. Sun et al. coated lithium-rich material with AlF_3 and they found that both the rate capability and the discharge capacity were improved [15]. Nevertheless, the coating layer formed by these materials usually increase the Li^+ -diffusion length, which is not conducive for Li^+ -ion conduction in the electrode. Furthermore, as insulators for Li^+ -ion conduction, these coating materials are unfavorable for the interfacial charge transfer of the cathode materials [23]. Li_2TiO_3 , as a novel coating material, has some unique advantages compared with the above mentioned materials. For instance, it has a three-dimensional path for Li^+ -ion diffusion [24], which can improve the efficiency of Li^+ -ion migration. The original characteristics of Li_2TiO_3 could not be changed in a wide voltage range and it could exhibit excellent structural stability in organic electrolyte [25,26]. Owing to the excellent characteristics Li_2TiO_3 has been applied to improve the electrochemical performances of LiMO_2 ($M = \text{Ni, Co and Mn}$) and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [23,27] as a new surface coating layer. However, to the best of our knowledge, there is no report about Li_2TiO_3 coating on the surface of lithium-rich layered oxide cathodes. Perhaps the reason lies in the structure complexity and formation difficulty of lithium-rich layered oxides. The traditional coating approaches including atomic deposition, sol–gel and mechanical mixing might not be used to uniformly coat Li_2TiO_3 on the surface of lithium-rich layered oxides [28–30].

In this study, we, for the first time, present a novel syn-lithiation strategy to successfully coat Li-rich layered $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ compound with a controllable and good physical contact layer of Li_2TiO_3 . The synthetic schematic illustration for Li_2TiO_3 coated Li-rich layered $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ is shown in Fig. 1. In this approach, $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ precursor is first prepared by a co-precipitation method. The reason we choose $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ as the precursors is that its dehydration reaction can occur at around 150 °C (see TGA curves in Figure SI 1). Subsequently, TiO_2 -coated $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}$ ($\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}@\text{TiO}_2$) is synthesized through a reaction between $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$, where $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ will lose part of crystal water during the reaction. The

Fig. 1. Schematic illustration of the preparation process for $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2@\text{Li}_2\text{TiO}_3$.

uniform TiO_2 coating on the surface of $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}$ is fabricated based on a subtle approach, where highly reactive $\text{Ti}(\text{OC}_4\text{H}_9)_4$ reacts with the released H_2O from $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ at 180 °C and a uniform TiO_2 coating layer forms. Finally, $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}@\text{TiO}_2$ is simultaneously lithiated to form Li_2TiO_3 -coated Li-rich layered oxide ($\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2@\text{Li}_2\text{TiO}_3$). Based on this method, we have prepared a series of Li_2TiO_3 -coated Li-rich layered $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ with different molar ratios of Li_2TiO_3 and comprehensively investigated the role of Li_2TiO_3 coating on the improvements of the electrochemical performances. Our studies show that the cycle stability and charge/discharge capacity of lithium-rich materials can be greatly improved by coating Li_2TiO_3 . And the Li_2TiO_3 coating layer also reduces the polarization of the electrode and retards voltage drop during cycling. In addition, the molar content of Li_2TiO_3 also has a significant influence on the electrochemical performances.

2. Experimental section

2.1. Materials preparation

2.1.1. Synthesis of $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ sample

$\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ sample was synthesized by a Co-precipitation (CP) method. Stoichiometric amounts of nickel (II) sulfate and manganese (II) sulfate were dissolved in deionized water. 2 M of $\text{Na}_2\text{C}_2\text{O}_4$ solution was added dropwise into the above solution under violently stirring. The mixed oxalate precursor was then filtered, washed, and dried overnight at 70 °C.

2.1.2. Synthesis of $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}@\text{TiO}_2$

A solvothermal process was carried out to coat different molar ratio TiO_2 on $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}$ samples. 1.2 mmol $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ was dispersed into 10 ml absolute ethanol, followed by addition of different molar ratio $\text{Ti}(\text{OC}_4\text{H}_9)_4$ diluted in absolute ethanol. The series of mixtures were maintained at 180 °C for 5 h. During the solvothermal process, the phase of

$\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ remain unchanged in addition to the loss of some H_2O . Then, the product of $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}@\text{TiO}_2$ was washed with ethanol, and collected by centrifugation.

2.1.3. Synthesis of Li_2TiO_3 -coated Li-rich layered $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ with different molar ratios of Li_2TiO_3 :

$\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}@\text{TiO}_2$ was dispersed in ethanol, and mixed with stoichiometric amounts of $\text{LiOH} \cdot \text{H}_2\text{O}$. The amounts of $\text{LiOH} \cdot \text{H}_2\text{O}$ is calculated by the following equation:

$$n_{\text{LiOH} \cdot \text{H}_2\text{O}} = 1.3n_{(\text{Ni}+\text{Mn})} + 2n_{\text{Ti}} \quad (1)$$

The mixture was first stirred under 80°C until it was dry, and then it was collected and calcinated at 800°C for 12 h with a heat rate of 5°C min^{-1} to get $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2@\text{Li}_2\text{TiO}_3$.

2.1.4. Synthesis of pristine $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ compound

In order to exclude the influence of the solvothermal process, the $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ sample is also maintained at 180°C for 5 h without addition of $\text{Ti}(\text{OC}_4\text{H}_9)_4$. Then the $\text{Ni}_{0.35}\text{Mn}_{0.65}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ sample is mixed with stoichiometric amounts of $\text{LiOH} \cdot \text{H}_2\text{O}$ and calcinated at 800°C for 12 h with a heat rate of 5°C min^{-1} to prepare pristine $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$.

2.2. Materials characterization

The crystal structures of the samples were characterized by X-ray diffractometer (Persee XD2) equipped with $\text{Cu-K}\alpha$ radiation ($\alpha = 1.5418$). Inductively coupled plasma (ICP) measurements were carried out on Agilent 7500ce. Particle morphologies of the prepared powders were observed by transmission electron microscopy. Energy dispersive X-ray spectroscopy (EDS) was carried out on OXFORD 7426 as the attachment of SEM, with the acceleration voltage of 20 KV. Thermogravimetric analyzer 2050 (TGA 2050) was applied on the metal oxalates precursors from room temperature to 600°C at a heating rate of 5°C/min under air flow. XPS spectra were obtained using a Kratos Axis ULTRA X-ray photoelectron Spectrometer under UHV conditions. In XPS, the energy of photoelectrons ejected when the sample is irradiated by soft X-rays (usually Al $\text{K}\alpha$) was analyzed.

2.3. Electrochemical measurement

A two-electrode cell was used in the electrochemical characterization by galvanostatic cycling. The composite positive electrodes were prepared by a slurry coating procedure. The slurry was made by mixing 82wt% active materials, 10wt% carbon black, and 8wt% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidinone (NMP). The slurry was spread uniformly on an aluminum foil current collector and dried under vacuum at 120°C for about 12 h. Then 2016-type coin cells were assembled in an Ar-filled glove box using Li foil as the counter electrode. The electrolyte was 1 mol/L LiPF_6 in a 1:1 mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) and the separator was Celgard 2500. Galvanostatic charge–discharge cycling was performed between 2.0 and 4.8 V (vs. Li/Li^+) using automatic galvanostat (NEWARE) at different current rates at room temperature. The electrochemical spectroscopy (EIS) was performed with an (PGSTAT 302N, Metrohm-Autolab) instrument using an amplitude of 5 mV and a frequency range from 100 kHz to 0.1 Hz.

3. Results and discussion

Fig. 2 shows X-ray diffraction (XRD) patterns of pristine and Li_2TiO_3 -coated [$\text{Ti}:(\text{Ni} + \text{Mn}) = 1, 3, 10, 15 \text{ mol}\%$] $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$

Fig. 2. X-ray diffraction patterns for different molar ratios of Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ powders.

samples. All the peaks can be well indexed to a hexagonal NaFeO_2 structure with space group R-3m and monoclinic system with space group C2/m [30–32]. The splitting of peaks corresponding to (006)/(102) and (108)/(110) planes are the signatures for the layered hexagonal type structure [33]. The ratio of the intensities of the two major peaks $I(003)/I(104)$ is a direct indication of cation mixing [34,35]. As can be seen from Fig. 2, the ratio of $I(003)/I(104)$ for all samples is less than 1.2 which means the rearrangement is existent between Li^+ and transition metal. And it is believed that cation mixing takes place during sintering when Ni^{2+} enters the Li^+ site causing small crystal distortions [36,37]. Weak superstructure reflection peaks appeared between 20° and 25° . They are characteristic of lithium-enriched nickel manganese oxides resulting from the ordering of metal ions (Li, Ni and Mn) in the transition metal layer of the layered lattice [38]. No impurity peaks corresponding to the Li_2TiO_3 -related compounds were observed in the XRD patterns. All the peaks are sharp and well defined suggesting that the compounds are generally well crystallized. In addition, it can be seen that the diffraction peaks of $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ shifted to lower 2θ angles with the increase in the amount of Li_2TiO_3 . The phenomenon can be ascribed to the reason that the radius of Ti atom is larger than that of Ni/Mn atoms and $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ unit-cells expand with Ni/Mn atoms replaced by Ti atom [39,40]. Furthermore, in order to identify the exact content of the components in the samples, the pristine and 3 mol% Li_2TiO_3 -coated lithium rich cathode materials were detected by inductively coupled plasma (ICP) measurements. It can be seen in Table SI 1 that the actual content of the elements is in good agreement with the theoretical content in the pristine and 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ materials. Therefore it can be concluded that the good lithiated phases can be prepared by the syn-lithiation strategy.

The SEM images of pristine and 3 mol% Li_2TiO_3 -coated materials were shown in Figure SI 2a and b, respectively. As can be seen from the SEM images, the average particle size is about 200–800 nm and all the particles are well-crystallized. The analysis reveals that the Li_2TiO_3 -coated and the pristine samples have the similar morphology, which suggests that the coating layer does not influence the powder morphology during the calcination at 800°C . In addition, in order to determine the presence of the various elements, the 3 mol% Li_2TiO_3 -coated sample was analyzed by EDS. As shown in Figure SI 2c, $\text{K}\alpha$ and $\text{K}\beta$ peak of the main elements of Ni and Mn ranged from 5.9 to 8.2 KeV, and the intensity of the peak is very high. Meanwhile, the $\text{K}\alpha$ and $\text{K}\beta$ peak of the Ti is located in the interval 4.3 to 5.0 KeV, which indicated the presence of Ti element clearly.

3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ sample was selected for further characterization. The TEM image in Fig. 3a clearly confirms the formation and presence of the Li_2TiO_3 coating layer on the surface of $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$. Fig. 3b shows an example of a primary particle that was completely surrounded by the Li_2TiO_3 coating layer, and the thickness of the coating layer is about 10–30 nm. Based on the synthetic process and TEM picture of the Li_2TiO_3 -coated material, we can speculate that there is a good physical contact between the host material and coating layer. Fig. 3c and d shows the line scan of the 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ sample. Elemental line scan for Ti, Mn, and Ni in Fig. 3d show the existence of Ti, Mn and Ni elements on the surface of the sample.

In order to clarify the surface elements composition and valence state of the nanoparticles, X-ray photoelectron spectroscopy (XPS) experiments were carried out for 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$. Fig. 4a shows the whole photoelectron spectroscopy of the 3 mol% Li_2TiO_3 -coated sample. The XPS spectra of $\text{Ni}2\text{p}_{3/2}$, $\text{Mn}2\text{p}_{3/2}$ and $\text{Ti}2\text{p}_{3/2}$ for the sample are given in Fig. 4b–d to further determine the oxidation states of these elements. The electron binding energies of the three elements and reference are listed in Table 1. In 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$, the $\text{Ni}2\text{p}_{3/2}$ peak is at 854.8 eV, and the $\text{Mn}2\text{p}_{3/2}$ peak is at 642.1 eV, which suggest that Ni and Mn ions are present as Ni^{2+} and Mn^{4+} , respectively. For the element of Ti, the $2\text{p}_{3/2}$ photoelectron energy is between +2 and +4. And the Ti^{4+} is the most stable form of existence for the element of Ti. The valence of the precursor of Ti is +4, and the Ti^{4+} is difficult to be reduced if there is no strong reducing agent. In addition, the $2\text{p}_{3/2}$ photoelectron energy of the Ti is very close to the energy of valence of +4. It can be judged that the valence of the Ti is +4, which is consistent with the existing form in the Li_2TiO_3 . As a result, the coated samples are described as surface- Li_2TiO_3 -rich nanoparticles.

To study the influence of Li_2TiO_3 coating on the cycling stability,

pristine and 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ cells with Li anodes were tested between 2.0 and 4.8 V at a current density of 100 mA/g after activation at 20 mA/g for 2 cycles. Fig. 5a shows the capacity stability over 100 cycles. The 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ electrode delivered approximately a discharge capacity of 105 mAh/g in a cut-off range between 2.0 and 4.8 V after 100 cycles. In contrast, the pristine sample delivered only 78 mAh/g discharge capacity under the same testing conditions after 100 cycles. In addition, the capacity retention of the uncoated and 3 mol% Li_2TiO_3 -coated sample is 73.3 and 87.1%, respectively. The results indicate that both the specific capacity and cycling performance are largely improved by Li_2TiO_3 coating. The reason is that Li_2TiO_3 as the coating layer improves the stabilization of the interface between the cathode and electrolyte [42,43] which could protect the Li-rich cathode materials against dissolution into the electrolyte. Fig. 5b and c shows the discharge curves of 3, 20, 50, 80 and 100 cycles for the pristine and 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$. With the increasing of the cycle, the discharging voltage plateau of the 3 mol% Li_2TiO_3 -coated electrode decreased slower compared with the pristine electrode. And it can also be clearly seen in Fig. 5d and e, there is a starting discharge voltage decline of the pristine electrode while there is almost no voltage decline of the 3 mol% Li_2TiO_3 -coated electrode. Fig. 5f and g shows the discharge curves for the pristine and 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ electrode at 3rd and 100th cycle. Comparing with the pristine electrode, the gap between the charge and discharge plateau region of the 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ is much smaller after 100 cycles. These results suggest that the 3 mol% Li_2TiO_3 -coated materials have very low polarization, and the charge–discharge process is nearly reversible. Many other materials, such as Sm_2O_3 , CaF_2 and Al_2O_3 et al., have been reported as a coating media to improve the electrochemical performance of the lithium rich materials [44–46]. But comparing with the Li_2TiO_3 , these materials almost did not play a role in

Fig. 3. a) TEM image of primary particles from 3 mol% Li_2TiO_3 -coated sample. b) The enlarged view of a portion from picture a. c, d) The line scan of the 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ powders.

Fig. 4. X-ray photoelectron spectroscopy (XPS) spectra of: a) all elements, b) Ni 2P_{3/2}, c) Mn 2P_{3/2} and d) Ti 2P_{3/2} for 3 mol% Li₂TiO₃-coated Li_{1.13}Ni_{0.30}Mn_{0.57}O₂ powders.

Table 1

The electron binding energies of the three elements and reference.

Elements	Ni	Mn	Ti
Reference (eV) [41]	+3:855.8–857.6	+4:641–642.5	+4:458.4–459.3
	+2:853.5–854.4	+3:641.2–641.7	+2:454.8–455.3
2P _{3/2} electron binding energies (eV)	854.8	642.1	457.9

reducing the electrode polarization. And at the current density of 100 mA/g, the discharge capacity of the Li₂TiO₃-coated lithium rich materials increased by 26%, while the Sm₂O₃ and CaF₂ coated lithium rich materials increased by only 5% and 10%, respectively. The reduced electrode polarization and larger increased discharge capacity of the Li₂TiO₃-coated electrode may be attributed to the reason that the Li₂TiO₃ coating layer compared with other coating materials has a three-dimensional path for Li⁺-ion diffusion, which can highly improve the efficiency of the Li⁺-ion migration [47].

The effects of Li₂TiO₃ coating molar content on the specific capacity and cycling stability have also been further investigated. Fig. 6a shows the reversible capacities of 0, 1, 3, 10, and 15 mol% Li₂TiO₃-coated samples as a function of the cycle number at the current density of 20 mA/g. The discharge capacities of 0, 1, 3, 10, and 15 mol% Li₂TiO₃-coated samples at the 50th cycle are 81, 152, 169, 155, and 153 mAh/g, respectively, (Table SI 2). This indicates that the specific capacity at the 50th cycle first largely increases and then decreases a little with the increase of Li₂TiO₃ coating as shown in Fig. 6b. The 3 mol% Li₂TiO₃-coated Li_{1.13}Ni_{0.30}Mn_{0.57}O₂ has the highest discharge capacity while the 10 mol% Li₂TiO₃-coated sample shows the highest capacity retention at the current density of 20 mA/g (Fig. 6b and c). The phenomenon reflects the competition between the following two factors. A thicker coating layer might more effectively prevent the cathode particles from reacting with the electrolyte solution and increases the stability of the structure, which improves the capacity retention of the samples. But Li₂TiO₃ is

not the active material and it doesn't contribute to the capacity itself. Too much Li₂TiO₃ coating will result in the loss of the capacity. Therefore, it is necessary to optimize the thickness of Li₂TiO₃ coating in the practical applications. Fig. 6d and e shows the charge–discharge curves of lithium-rich materials at 1st and 50th cycle. Similar to other Li-enriched cathodes, the cells made with pristine and Li₂TiO₃-coated Li_{1.13}Ni_{0.30}Mn_{0.57}O₂ electrodes exhibited a voltage plateau around 4.5 V, which is related to the concomitant extraction of lithium and oxygen from the Li₂MnO₃ host structure during the initial charging [7,20,48–50]. All the electrodes showed long plateau above 4.5 V, and it is irreversible in the following cycles. Recent study showed that the irreversible capacity of the plateau at about 4.5 V is related to the oxygen loss during the first charging [51]. The 1 mol% and 3 mol% Li₂TiO₃-coated samples delivered discharge capacity of 230 mAh/g and 218 mAh/g initially at the current density of 20 mA/g, while the pristine electrodes delivered the discharge capacity of 205 mAh/g initially. And the 10 mol% and 15 mol% Li₂TiO₃-coated lithium-rich materials show the lower discharge capacity compared with the pristine electrodes. The reason, which has been mentioned in the above section, is that too much coating amount of inactive Li₂TiO₃ will reduce the capacity of the cell.

In order to investigate the effect of Li₂TiO₃ coating layer on the rate capability, 3 mol%-Li₂TiO₃ coated electrode and pristine electrode were cycled between 2.0 and 4.8 V at various current densities, as shown in Fig. 7a. The cycle life curves for 3 mol%-Li₂TiO₃

Fig. 5. a) Plots of specific discharge capacity vs. number of cycles for the pristine and 3 mol% Li_2TiO_3 -coated electrode at a current density of 100 mA/g b, c) Discharge curves of 3, 20, 50, 80 and 100 cycles at current density of 100 mA/g for the pristine and 3 mol% Li_2TiO_3 -coated electrode. d, e) The variation trend of starting discharge voltage after different cycles for the pristine and 3 mol% Li_2TiO_3 -coated electrode. f, g) Specific capacity vs. voltage curves for the pristine and 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ electrode at 3rd and 100th cycle.

coated electrode and pristine electrode recorded at 0.2C (40 mA/g) current rate for one to six cycles, 0.4C (80 mA/g) current rate for 7–12 cycles, 0.8C (160 mA/g) current rate for 13–18 cycles, 1C (200 mA/g) current rate for 19–24 cycles, 1.5C (300 mA/g) current rate for 25–30 cycles and 2C (400 mA/g) current rate for 31–36 cycles. It can be seen from Fig. 7a that 3 mol%- Li_2TiO_3 coated electrode showed higher discharge capacity than un-coated electrode at each current density, especially in the large current density. Fig. 7b and c showed the charge–discharge curves of the pristine electrode and 3 mol%- Li_2TiO_3 coated material at various rates, respectively. The uncoated and 3 mol%- Li_2TiO_3 coated

$\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ delivered discharge capacities of 142 mAh/g and 158 mAh/g, respectively, at the current density of 40 mA/g. And with the increase of current density the capacity difference becomes larger. More specifically, at the current density of 200 mA/g, the uncoated and 3 mol%- Li_2TiO_3 coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ delivered discharge capacity of 97 mAh/g and 119 mAh/g, respectively. The 3 mol%- Li_2TiO_3 coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ delivered discharge capacity of 92 mAh/g at the current density of 400 mA/g, while the pristine electrode delivered discharge capacity of only 60 mAh/g. The results show that the Li_2TiO_3 -coated lithium rich materials exhibit a great rate performance. Additional, the XRD of

Fig. 6. a) Plots of specific discharge capacity vs. number of cycles for the different molar ratio of Ti:(Ni + Mn) Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ powders at the current density of 20 mA/g b) Plots of specific discharge capacity vs. different molar ratios of Ti:(Ni + Mn) Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ powders. c) Plots of capacity retention vs. different molar ratio of Ti:(Ni + Mn) Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ powders. d) Specific capacity vs. voltage curves for the different molar ratio of Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ powders at first cycle. e) Specific capacity vs. voltage curves for the different molar ratio of Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ powders at 50th cycle.

Fig. 7. a) The capacity retention of un-coated and 3 mol%- Li_2TiO_3 coated cells during cycling at various rates in the voltage range of 2.0–4.8 V at room temperature. The charge–discharge curves of $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ cells at various rates between 2.0 and 4.8 V: b) The un-coated, c) 3 mol%- Li_2TiO_3 coated. d) Nyquist plots for 3 mol%- Li_2TiO_3 coated electrode and pristine material, with the equivalent circuit as the inset.

the Li_2TiO_3 -coated materials demonstrated that there is titanium substitution on the host materials and it has been reported that the substitution of titanium could improve the structural stability of

layered rocksalt type cathodes materials [40,52–54]. The better cyclic stability of the Li_2TiO_3 -coated materials compared with the pristine material can be attributed to the Ti substitution and Li_2TiO_3

coating layer on the host material. Specifically, the Ti substitution results in the suppression of transition metal ions dissolution [40] while Li_2TiO_3 coating layer suppressed the side reactions of the host material with electrolyte, which could both enhance the cycling stability of the lithium rich cathode materials. And it is suggested that the Ti substitution hardly play a role in improve the rate capability of the lithium rich materials [40]. The highly enhanced rate performance of the lithium rich cathode materials in this work is mainly duo to the Li_2TiO_3 coating layer which is favorable for the Li^+ ion migration. Meanwhile, the Li_2TiO_3 coating layer also reduces the polarization of the electrode and retards voltage drop during cycling. Due to these reasons, it can be concluded that the ionic conductivity of Li_2TiO_3 leads to high electrochemical performance of the lithium rich cathode materials.

In addition, the difference in resistance between the coated and pristine electrodes has been revealed by electrochemical impedance spectroscopy (Fig. 7d). The Nyquist plots of both materials show the similar equivalent circuit. And it can be clearly seen in Table SI 3 that the charge transfer resistances for the 3 mol% Li_2TiO_3 -coated material (308.67Ω) is smaller than the uncoated material (380.96Ω), which indicates that the Li_2TiO_3 coating layer effectively reduces the barrier for Li^+ -ion transfer at the electrode-electrolyte interface. The excellent rate capability and the reduced charge transfer resistance of the coated Li-rich layered oxide material can be attributed to the synergetic effect of the following factors: the integrity of conductive Li_2TiO_3 coating layer, the improved ionic conductivity of Li_2TiO_3 and the three-dimensional path for Li^+ -ion diffusion. These unique advantages improve the velocity of Li^+ -migration on the surface of the electrode and further enhance the reversible capacity and rate performance of lithium-enriched materials.

4. Conclusions

In conclusion, a series of Li_2TiO_3 -coated Li-rich layered cathode materials with different molar ratios of $\text{Ti}:(\text{Ni} + \text{Mn})$ have been successfully prepared by a subtle coating approach. The coated samples show enhanced capacity and rate capability in compared to the pristine sample and the coating amount of Li_2TiO_3 also has a large influence on the electrochemical performances. In addition, the Li_2TiO_3 coating layer also reduces the polarization of the electrode and retards voltage drop during cycling. The capacity of 3 mol % Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ at the 100th cycle is much higher than that of the pristine electrode. The rate capability of 3 mol% Li_2TiO_3 -coated $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ at 1C and 2C are enhanced by 18.5% and 34.8%, respectively. Li_2TiO_3 -coating has been found an effective method to improve the electrochemical performances of lithium-rich layered oxides cathode material. Moreover, Li_2TiO_3 , as an impressive coating material, might also be applied to enhance the electrochemical properties of other cathode and even anode materials for high performance Li-ion batteries.

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