



# Synergistic effects of ion doping and surface-modifying for lithium transition-metal oxide: Synthesis and characterization of La<sub>2</sub>O<sub>3</sub>-modified LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>

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## ABSTRACT

It is highly desirable to improve the high voltage stabilities of cathode materials for Li-ion battery materials since it can deliver a higher reversible capacity at high cutoff voltage. Herein, we propose a novel facile strategy to generate La<sub>2</sub>O<sub>3</sub>-modified LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> with superior electrochemical performance in the voltage range of 2.5–4.5 V via a solid-state method. It can be observed that La<sub>2</sub>O<sub>3</sub>-modified LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> can greatly enhance the electrochemical performance due to the synergistic effect of ion doping and surface-modifying. La ions doping can alleviate the Li<sup>+</sup>/Ni<sup>2+</sup> mixing, and substantially enhance the structure stability of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> during charge/discharge cycles at high cutoff voltage. LaNi<sub>0.4</sub>Co<sub>0.6</sub>O<sub>3</sub>/LaMnO<sub>3.26</sub> spreading on the surface layer is very useful in improving the diffusion of Li<sup>+</sup> and inhibiting the particles from reacting with the electrolyte, enhancing the high voltage stabilities of the interface between electrode and electrolyte. The capacity retention of 0.7% (molar fraction) La<sub>2</sub>O<sub>3</sub>-modified LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> is 79.0% after 300 cycles compared to 61.7% for bare LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>. And its discharge capacity at 10 C is 141.7 mAh g<sup>-1</sup> in the voltage range of 2.5–4.5 V, which is higher than those of other samples. This work not only offers a facile novel strategy to achieve superior electrochemical performances of cathode materials but also presents some new insights into the stabilization mechanism of modified cathode materials during charge/discharge cycles or long-term storage at high cutoff voltage.

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## 1. Introduction

The growing demand for a multitude of emerging applications, ranging from portable electronic devices to electric vehicles, has promoted the development of high energy density and long cycle life for rechargeable batteries [1–3]. Lithium-ion batteries, lithium oxygen batteries and lithium-sulfur batteries, as the promising electrochemical energy storage systems have been widely investigated. However, lithium oxygen batteries and lithium-sulfur

batteries suffer from several fundamental challenges in the face of the applications of these materials, including security, practicability etc. [4–11] Significant progress has been made in lithium-ion batteries (LIBs) for applications in electric vehicles and grid energy storage. Although after several decades of research, cathode materials are still considered a major limiting factor in the applications of LIBs. In the past few decades, LiCoO<sub>2</sub> has been the dominant cathode material for LIBs due to its simple preparation and stable electrochemical cycling performance in low voltage. But the utilization of lithium ions in LiCoO<sub>2</sub> cathode material is limited to only 50% for acceptable electrochemical performance, which corresponded to its practical specific capacity at only 140 mAh g<sup>-1</sup> [12,13]. The layered transition-metal oxides (Li [Ni<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>]O<sub>2</sub>, NCM, or NCM<sub>xyz</sub>) are regarded as an alternative cathode materials that offer high specific capacity, relatively low-cost cathode and low

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toxicity compared to LiCoO<sub>2</sub> in rechargeable Li-ion batteries. In Li [Ni<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>]O<sub>2</sub> group, LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (NCM) has been hotly studied owing to the superior charge/discharge properties. Usually, those cathode materials possess great cycle stabilities at low cutoff voltage of 4.2 or 4.3 V, but unfortunately the utilization of Li<sup>+</sup> in cathode material is limited at such lower cutoff voltage, resulting in the lower capacity. Therefore, its high cutoff voltage performances have to be investigated to obtain higher capacity. However, those materials suffer from many challenges in high cutoff voltage, such as the migration of transition metal ions into Li<sup>+</sup> vacant sites at the highly delithiated state result in structural instability of those cathode materials, and the cathode degradation reaction with HF in electrolyte [14,15] leads to its capacity fades upon the prolonged charge/discharge cycling, and its poor rate capability due to low electronic and ionic conductivity and Li/Ni cation mixing [16–18]. So, improving the high voltage stabilities of the cathode materials is conducive to increasing the reversible voltage window and thus the attainable capacity of Li-ion batteries.

In order to address those problems, researchers have attempted a series of modification measures to promote high cutoff voltage electrochemical performance of NCM including ion doping and surface coating. Doping with metal or non-metallic ions on the surface and into the bulk phase can improve the stability of the material structure concurrently. Lin, Y [19] studies that the extracting efficiency of lithium ions can be enhanced by doping aluminum ions. It is known that the larger ionic radii of Na<sup>+</sup> [20], K<sup>+</sup> [21] and La<sup>3+</sup> [22,23] ions have been successfully doping in layered oxides cathode materials, and those ions with ionic radii larger than 0.100 nm may expand and stabilize the pathway for intercalation/deintercalation of Li<sup>+</sup> resulting in the enhancement of rate capability and the suppression of voltage and capacity fading during cycling. And there are also some other doping elements such as Ti [24,25], Mo [26], Sn [27] and F [28] used in modifying materials. However, metal dopants are often reported to play a limited role in preventing surface Li or transition metal (TM) ion dissolution at high cutoff voltage, ascribed to the presence of HF and related acids in the liquid electrolyte. A proper coating layer can not only protect the electrode surface from direct contact with the electrolyte, but also suppress the side reactions between the electrolyte and electrode in high cutoff voltage. The coating layers such as MgO [29], LiF [30], LaF<sub>3</sub> [31], LiFePO<sub>4</sub> [32] and carbon [33] may effectively improve the cycle performance and thermostability of materials [34]. But unfortunately, the cycle property of NCM can be improved by coating at the expense of capacity more or less. In order to better adapt to the commercial application, this coating material should have high electronic and ionic conductivity to enhance the rate capacity and cycle performance. The recent theoretical studies have suggested that “trivalent oxides” (such as La<sub>2</sub>O<sub>3</sub> [35,36], Al<sub>2</sub>O<sub>3</sub> [37,38]) are ‘more’ promising coating materials, compared to other candidates, because these coating materials have the potential to prolong the cycle-life of Li-ion batteries and surpass the performance of common coatings based on conventional materials.

It's critical to improve high voltage stabilities of cathode materials for increasing the reversible voltage window and thus the attainable capacity of Li-ion batteries. Herein, we propose a novel facile strategy to generate the La<sub>2</sub>O<sub>3</sub>-modified NCM material with superior rate capacity and cycle performance at high cutoff voltage via a solid-state method. It is proved that the surface modified NCM material by La<sub>2</sub>O<sub>3</sub> can enhance the rate capacity and cycle performance of the materials at high cutoff voltage, due to the synergistic effect of ion doping and surface modifying. La ions doping can alleviate the Li<sup>+</sup>/Ni<sup>2+</sup> mixing, and substantially enhance the structure stability of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> during charge/discharge cycles in high cutoff voltage. LaNi<sub>0.4</sub>Co<sub>0.6</sub>O<sub>3</sub>/LaMnO<sub>3,26</sub> spreading on surface layer is very useful in improving the diffusion of Li<sup>+</sup> and

inhibiting the particles from reacting with the electrolyte, enhancing the high voltage stabilities of the interface between electrode and electrolyte. Here, the fabrication and electrochemical behavior of NCM-La are discussed in detail.

## 2. Experimental section

### 2.1. Materials preparation and characterization

The precursor (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)(OH)<sub>2</sub> powder was produced via a co-precipitation method, as our previous work [39]. All reagents used were analytically pure. The synthesis process is as follows: stoichiometric amounts of the soluble salts, NiSO<sub>4</sub>·6H<sub>2</sub>O, CoSO<sub>4</sub>·7H<sub>2</sub>O, and MnSO<sub>4</sub>·H<sub>2</sub>O were dissolved in deionized water by magnetic stirring to form a 2.0 M TM solution. NaOH and NH<sub>4</sub>OH were also dissolved in distilled water to form a 4.0 M solution. Then those two kinds of solution were simultaneously pumped into a continuous reactor with continuous stirring for 3 h under 55 °C Ar atmospheres. The homogeneously precipitated hydroxide powder (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)(OH)<sub>2</sub> was filtered off and dried at 120 °C overnight.

The bare NCM and La<sub>2</sub>O<sub>3</sub>-modified NCM were obtained via a solid-state method. The precursor (Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)(OH)<sub>2</sub> powder was mixed with Li<sub>2</sub>CO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>, and the molar ratio of (Mn + Ni + Co)/Li/La = 1:1.05:0, 1:1.05:0.002, 1:1.05:0.005, 1:1.05:0.007, 1:1.05:0.01 and 1:1.05:0.02. The excess in Li is intended to compensate the loss of lithium through evaporation during the calcinations. After suitable grounding and stirring, the mixtures were pressed into a sheet at 20 MPa. Then the mixtures were initially heated to 500 °C for 5 h to melt the lithium salt and were subsequently calcined at 900 °C for 12 h. The obtained compound was named as NCM-La-0%, 0.2%, 0.5%, 0.7%, 1.0% and 2.0%, respectively.

The crystal structure of the as prepared cathode materials was performed on Rigakud/MAX-2500/pc X-ray diffraction (XRD) with Cu Kα radiation. The XRD data were analyzed by Rietveld refinement method using Rietica software to obtain detailed crystal information. General data for the Rietveld analysis was collected by a step-scan method with measurement conditions: 2θ = 10–80°, 2 s per step, and 0.02° per step. The degree of the refinement was judged by S (S = Rwp/Re, where Rwp was the residue of the weighted pattern and Re was the statistically expected residue value). The field-emission scanning electron microscopy (FESEM) on an S-4800 microscope was used to characterize the morphology of the obtained samples.

### 2.2. Electrochemical measurements

The working electrodes were prepared by the slurry coating procedure. Mixing 80 wt% active material with 10 wt% carbon black as conductive agents and 10 wt% polyvinylidene fluoride (PVDF) as a binder in N-methyl-2-pyrrolidone (NMP) solvent, and then the slurry was uniformly spread onto the Al foil. The foil was dried at 120 °C overnight and punched into discs of with 10 mm diameter. Since the mass loading of active materials on the electrode plays an important role in the electrochemical performances [40–42]. In our report, the mass loading of the active cathode materials on the aluminum foil is average 1.5 mg cm<sup>-2</sup>. The as-prepared electrodes were assembled with Li electrodes and electrolyte into CR2032-type coin cells in an argon-filled glove box for the future electrochemical test. The electrolyte employed was a solution of 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate and diethyl carbonate with 1:1 vol ratio. A microporous polypropylene film (Celgard 2400) was used as the separator. The cells were tested by galvanostatic charge/discharge cycling on a battery testing system (LAND, Wuhan, China)

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