



Beneficial effect of incorporating Ni-rich oxide and layered over-lithiated oxide into high-energy-density cathode materials for lithium-ion batteries

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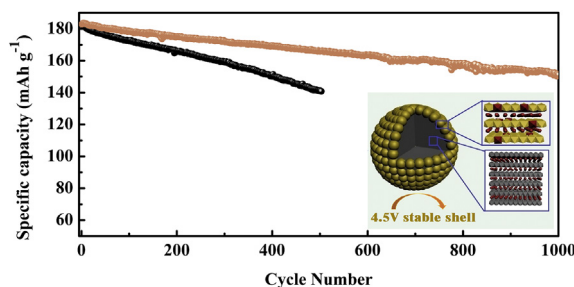
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HIGHLIGHTS

- A novel layered over-lithiated oxide coating technique has been introduced.
- Heterostructured NCA@LLO composite has been constructed successfully.
- LLO surface restrains the formation of residues on NCA during cycling.
- 4.5 V stable over-lithiated surface improves the thermal stability of NCA.

GRAPHICAL ABSTRACT



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ABSTRACT

Layer structured Ni-rich oxides with high energy density suffer from an aggressive side reaction at the deep-charged state, resulting in consequent structure collapse and capacity fading. Herein, a facile modification strategy has been developed by designing electrochemically stable lithium-rich layered oxides as the shell and high-energy-density Ni-rich oxides as the core. Mn^{2+} , Co^{2+} , and Ni^{2+} solutions are introduced to form $\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}(\text{OH})_{1.6}$, which is homogeneously coated on $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ composite. Materials incorporating advantages of Ni-rich oxides and layered over-lithiated oxides are obtained after simple heat treatment. $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ coating improves the cycling performance of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ pronouncedly even at a high cut-off voltage. 1% layered over-lithiated oxide modified materials show discharge capacities of 196.6, 188.8, and 182.9 mAh g^{-1} at the rates 0.2, 0.5, and 1 C, respectively, in square full-cells between 2.8 and 4.35 V, and display an improved cycling performance with 82.6% capacity retention during 1000 cycles at 1 C rate.

1. Introduction

Layer structured $\text{LiNi}_{1-a-b}\text{Co}_a\text{Al}_b\text{O}_2$ ($0.5 < 1-a-b < 1$) is one of the most promising cathode materials for advanced lithium-ion batteries (LIBs) for applications in smart grids, portable storage and electric

vehicles owing to its high energy density, environmental friendliness and relatively low price [1,2]. However, Ni^{4+} ions directly in contact with electrolyte at charged state are chemically unstable, which results in rapid irreversible capacity fading and thermal run away during long-term cycling at a high delithiated state [3,4]. Additionally, the Li-based

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residues produced from Li_2O species reacting with H_2O and CO_2 in ambient atmosphere on $\alpha\text{-NaFeO}_2$ structured Ni-rich oxides lead to poor Li^+ storage property of those cathodes [5,6]. Thus, the initial surface chemical properties of active particles play a critical role in the development of Ni-rich cathode materials. Developing architecture with the necessary cost-effective, practical, and robust characteristics remains a serious challenge when producing cathode materials with superior lithium ion storage properties [7–9]. So far, effective results have been obtained by using various methods, such as metal compound coating [10,11], core-shell structure designing [12–16], and elemental gradient doping [2,9,17,18]. However, most of these modified materials hardly act as a protective layer and a Li^+ conductor at high voltage state simultaneously. Lithium-rich layered oxides (LLO), within the system of $x\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 \cdot (1-x)\text{LiMO}_2$ (M is one or more transition metals), are considered as another kind of high-energy-density cathode materials for LIBs [19–21]. The most attractive property of LLO is their very high capacity ($\sim 250 \text{ mAh g}^{-1}$) when charged to 4.6 V or higher. The discharge capacity of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ series of oxides reaches up to 300 mAh g^{-1} and shows good structural stability at a voltage of 4.8 V [22–24]. However, their poor cyclic stability, high electronic/ionic impedance, and voltage fading restrict their wide application in practice. In addition, these cathodes exhibit a relatively high capacity only when charged up to 4.6 V, usually followed by remarkable electrolyte oxidation and serious transition metal ion dissolution [25,26]. However, from another point of view, owing to its electrochemical activity, good structural stability at high voltage in the voltage range 2.8–4.5 V, good safety performance ($< 4.5 \text{ V}$), and ease of synthesis, LLO is a promising candidate for constructing a stable surface structure of Ni-rich layered cathode materials. Li et al. [18] and Song et al. [16] combined Ni-rich composition and Li_2MnO_3 to balance the advantages and disadvantages of these materials in a hybrid system. Thus, a new method for designing cathodes with high energy density and high stability has been proposed by incorporating the advantages of Ni-rich oxides and layered over-lithiated oxides. Herein, we attempt to design high-voltage layered $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ on Ni-rich layered oxides. If LLO is uniformly coated on Ni-rich layered oxides as capsule shells, the reaction between Ni-rich oxides and electrolyte during cycling will be passivated and the unobstructed transferring network for Li^+ will be reserved, thus, improved electrochemical performance can be expected. In this paper, we report a Ni-rich layered cathode material with improved performance via LLO coating. The $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) materials are synthesized via a simple and efficient precipitation method described in our previous reports [17,27–29]. As shown in Fig. 1, $\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}(\text{OH})_{1.6}$ is preferentially precipitated on the surface of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ once Mn^{2+} , Co^+ , and Ni^{2+} solutions are added to the intensely stirred NCA slurry. Subsequently, commonly used O_2 -rich heat treatment is introduced to synthesize high crystallized $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ -coated $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ composites with high crystallinity. In this work, the synthetic method, electrochemical performance, and structural stability of LLO-modified materials are discussed in detail.

2. Experimental

NCA cathode materials were synthesized via a commonly used O_2 -rich heat treatment by using spherical $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$ precursors according to our recent report [17]. To prepare $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ -modified $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ samples, $\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}(\text{OH})_{1.6}$ -coated $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ precursors were synthesized first. As shown in Fig. 1, stoichiometric amounts of Ni (NO_3) $_2 \cdot 6\text{H}_2\text{O}$, Co(NO_3) $_2 \cdot 6\text{H}_2\text{O}$, and Mn(NO_3) $_2 \cdot 6\text{H}_2\text{O}$ were dissolved in ethyl alcohol, to modulate the concentration of $\text{M}(\text{Mn}^{2+} + \text{Ni}^{2+} + \text{Co}^{2+})$ to 1 mol L^{-1} . Subsequently, 100 g of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder was dispersed into 200 g of ethyl alcohol uniformly via mechanical agitation at a stirring rate of 500 rpm during hydroxide coating process. The reaction temperature was controlled to be $40 \text{ }^\circ\text{C}$, the ionic

mixed solution was pumped into the above system with a constant speed of 2 mL min^{-1} and the lower limiting value of pH of the system was controlled to be 10.00 ± 0.05 using 1 M LiOH alcohol solution. The precursors were obtained after washing and filtering for three times, followed by drying at $120 \text{ }^\circ\text{C}$ in a vacuum oven for 24 h. In this work, we used ethyl alcohol as the washing medium. Subsequently, the precursors were mixed with stoichiometric sub-micron-sized $\text{LiOH} \cdot \text{H}_2\text{O}$ thoroughly and sintered at $750 \text{ }^\circ\text{C}$ for 2 h under oxygen flow. Finally, black $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ -coated $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders (Marked as LLO@NCA) were obtained. For comparison, 1 wt% $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ -coated $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (1%LLO@NCA) and 10 wt% $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ -coated $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (10%LLO@NCA) materials were prepared.

The button battery preparation, 1Ah square full-cell package, elemental composition analysis, crystal structure characterization, morphology characterization, electrochemical tests, and differential scanning calorimetry (DSC) measurement were performed according to our previous report [29].

3. Results and discussion

One of the fundamental problems of NCA is its rapid reaction with air resulting in the formation of Li-based alkaline residues on the outer surface. Here, we used a suitable metal ionic alcohol solution as a substitute for water, which is commonly used for washing, to synthesize NCA cathode materials with improved performance. The change in the crystal structure and elementary chemical evolution of the samples were investigated using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Fig. 2 (a) shows the XRD profiles of the pristine NCA and the materials modified with 1 wt% LLO and 10 wt% LLO. The diffraction peaks of all the samples match well with the standard pattern of layer-structured lithium nickel oxides, the patterns were identified as a hexagonal $\alpha\text{-NaFeO}_2$ structured ($\text{Li}_{0.99}\text{Ni}_{0.01}$) ($\text{Ni}_{0.798}\text{Co}_{0.202}$) O_2 , PDF #87-1562, belonging to the R-3m space group. This confirms that LLO modification does not disturb the layered structure of the bulk phase. LLO characteristic peaks are too weak to be identified in the sample coated with 1 wt% LLO. As the coated LLO ratio is increased to 10 wt%, peaks attribute to monoclinic unit cell C2/m caused by lithium entering the transition metal layer are observed between 20° and 25° as shown by amplified patterns in Fig. 2 (b) [24]. Fig. 2 (c) shows the XRD patterns of pure $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ synthesized by using the same precipitation and calcination principle. It can be observed that all the diffraction peaks belonging to the $\alpha\text{-NaFeO}_2$ phase attributed to the R-3m space group, and the peaks corresponding to the monoclinic unit cell C2/m identified as Li_2MnO_3 (PDF# 27-1252) structure can be observed between 20° and 25° , demonstrating the perfect formation of over-lithiated oxide in this work [30]. The X-ray Rietveld refinements of NCA and 1%LLO@NCA are performed using GSAS/EXPGUI software and the results are collectively shown in Table S1 and Fig. S1. It is evident that, the strong and sharp diffraction peaks, $\sim 0.5\%$ of Ni-Li ion mixing and their negligible difference in lattice parameters (Table S1), in addition to a clear splitting between the (006)/(102) and (108)/(110) reflection peaks of both samples indicate the same crystal structure (PDF #87-1562, belonging to R-3m space group) of NCA and 1%LLO@NCA. Thus, both XRD and Rietveld refinement results prove that LLO modification doesn't change the layered structure of the bulk phase.

To further discuss the structure of the LLO@NCA composite, XPS for Ni_{2p} , Co_{2p} , Mn_{2p} and O_{1s} on the surface of LLO@NCA is conducted. No apparent difference in the oxidation states of Ni is identified, however, the binding energy gap between $\text{Ni}_{2p_{3/2}}$ and $\text{Ni}_{2p_{1/2}}$ is enlarged as the LLO quantity increased, and the value for 10% LLO@NCA is approximately 17.82 eV, which is almost the same as that of the pure LLO sample. This illustrates that the chemical state of Ni on the surface of LLO-modified samples was similar to Ni in the over-lithiated oxides. The shapes of Co_{2p} (Fig. 2 e) spectra for the pristine, 1%LLO@NCA,

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