



Stable interstitial layer to alleviate fatigue fracture of high nickel cathode for lithium-ion batteries



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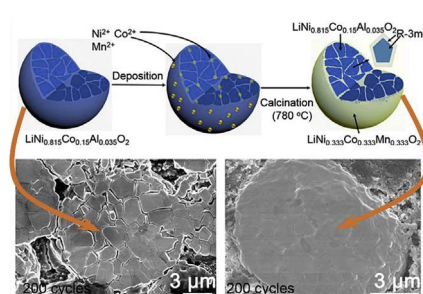
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HIGHLIGHTS

- The high-Ni cathode was treated by an interstitial coating without capacity loss.
- The interstitial layer imparts high capacity retention of 88.5% after 200 cycles.
- The coated particles show structure integrity other than cracking.
- The morphology degradation is a fatigue process within long-term cycling.
- The coated cathode has an excellent elastic recovery leading to long cycle life.

GRAPHICAL ABSTRACT



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ABSTRACT

High nickel cathodes can deliver higher capacity with lower cost than conventional LiCoO_2 , however, the irreversible structural and morphology degradation with long-term cycling hinder their further application. In this paper, $\text{LiNi}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}\text{O}_2$ agglomerates are treated by $\text{LiNi}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333}\text{O}_2$ coating to get a stable interstitial layer without capacity loss. The interstitial layer is about 10 nm in thickness and has a layered (R-3m) structure, which can improve the chemical and mechanical stability of cathode materials with capacity retention of 88.5% after 200 cycles. The structural analysis and *in-situ* compression test proves that the morphology degradation is a fatigue process within long-term electrochemical reaction, and the coated sample has an excellent elastic recovery capacity thus leading to long cycle life.

1. Introduction

With the expansion of hybrid electric vehicles (HEVs) and electric

vehicles (EVs), the next generation lithium-ion batteries (LIB) demand cathode materials with higher capacities and better cycling stability [1]. Developing prominent cathodes with high energy density and high

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power density has been raised and carried out by many researchers. High-Nickel cathodes, such as $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ [2], $\text{LiNi}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}\text{O}_2$ [3] are considered as promising candidates to meet the increasing energy density requirements due to their high specific capacity and high power density [4].

However, the main challenges for the high nickel cathodes still exist on the drastic structural degradation and poor cycling performance caused by the repeating lattice change during lithiation/delithiation and harmful side reactions on the surface [5]. Tremendous attempts have been conducted to eliminate above issues [6–8]. The well-designed ion doping and surface-coating strategies have been reported intensively, however, little emphasis has been put on reducing the inner stress of cathode material caused by phase transition with lithium intercalation/deintercalation [9].

In our previous work, we have carried out a systematic investigation on the inner structure of the high nickel cathode material, and found that the secondary structures (i.e. the arrangement of primary particles) had great influence on the physical and electrochemical properties, such as sintering property, rate performance and cycle life [10]. During charging and discharging, internal stress in cathode material is generated because of the interaction of lithium ions with the lattice structure. The stresses induced by the electrochemical reaction may cause irreversible damage to the secondary structure and accelerate side reactions with the increasing surface area owing to the formation of cracks [1,11]. Although there are some methods reported to address the morphological degradation, the influence of *in-situ* stress on cathode materials is not studied yet.

Here, we modified the surface of $\text{LiNi}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}\text{O}_2$ (abbreviated as NCA) agglomerates by forming a stable layer of $\text{LiNi}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333}\text{O}_2$ (NCM333) as interstitial coating without capacity loss. The design strategy is multifold: First, the interstitial layer has higher content of Mn and Co than that in the bulk thus can provide more stable surface towards electrolyte. Secondly, the lattice matching between the interstitial layer and bulk material can lease the boundary stress. Third, unlike surface coating, the interstitial layer could protect the inner primary particles other than merely the outer surface of the secondary particle. The electrochemical performances of the hybrid cathode materials would be improved due to the formation of a stable interstitial layer. Stable cycling performance is demonstrated for 200 cycles with the capacity retention of 88.5%. The coated sample also show superior storage performance compared to the bare NCA cathode. In addition, we combined *in-situ* stress measurement and electrochemical test to reveal the underlying mechanism of the morphological degradation and further demonstrated the superiority of the interstitial coating.

2. Experimental

2.1. Synthesis of NCA and NCA-NCM cathode materials

The spherical precursor $\text{Ni}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}(\text{OH})_2$ was synthesized by a modified co-precipitation method [1]. Briefly, proper amounts of NiSO_4 , CoSO_4 and AlSO_4 (cationic ratio of Ni: Co: Mn = 815:150:35) were added to a strongly stirred tank reactor under nitrogen atmosphere, forming a 2.0 mol L^{-1} solution. A 2.0 mol L^{-1} ammonia as a complexation agent and a 4.0 mol L^{-1} NaOH solution as precipitate agent were also pumped into the reactor at the same time. The obtained precursor was then dried at $120 \text{ }^\circ\text{C}$ for 4 h in the air. After drying, the precursor and $\text{LiOH}\cdot\text{H}_2\text{O}$ were ball milled for 4 h to make uniform mixture. The Li/TM molar ratio of mixture was fixed at 1.05 [12,13]. The mixture was heated to $550 \text{ }^\circ\text{C}$ at a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$, then heated to $780 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ and finally calcined for 10 h in the O_2 . The NCA-NCM sample was prepared in a 40 ml ethanol solution of 2 wt % $(\text{CH}_3\text{COO})_2\text{Co}$, $(\text{CH}_3\text{COO})_2\text{Mn}$, and $(\text{CH}_3\text{COO})_2\text{Ni}$. 10 g of the NCA cathode was added to the solution. The mixed solution was stirred at $60 \text{ }^\circ\text{C}$ until the solvent completely evaporated. The surface

treated samples were then calcinated at $780 \text{ }^\circ\text{C}$ for 5 h in O_2 .

2.2. Materials characterization

The sample structures were identified by powder X-ray diffraction (XRD, Cu $\text{K}\alpha$ radiation, Bruker D8 Advance). X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., Axis Ultra) was performed to compare the valence state of the elements. The peak fitting of Ni 2p was based on following guidelines: the area ratio of Ni 2p_{3/2} to Ni 2p_{1/2} was constraint at 2:1; the half-peak width was constraint the same for a pair of peaks. The morphology and element distribution were analyzed using scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy dispersive spectrometer (EDS, Horiba, EX-250) and a field-emission high resolution transmission electron microscope (HRTEM, JEM-2100F). The cross-sectional SEM samples were prepared by a low-energy Ar-ion milling system (Gatan Model 691PIPS).

2.3. Electrochemical tests

The working electrode was prepared by mixing active material (90 wt%), carbon black conductive additive (Super P, 5 wt%), and polyvinylidene fluoride binder (PVDF, 5 wt%) dissolved in N-methylpyrrolidone (NMP). The slurry was then casted on aluminum foil and followed by drying at $120 \text{ }^\circ\text{C}$ for 24 h in vacuum oven. Electrolyte was a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) containing lithium hexafluorophosphate (LiPF_6). Celgard 2400 film was used as the separator. The cells were assembled in an argon-filled glove box with H_2O and O_2 concentrations below 0.01 ppm. All the electrochemical performance was performed on a LAND CT2001C battery test system (Wuhan, China) between 2.8 and 4.25 V at different charge/discharge rates (1 C = 160 mA g^{-1}) at $25 \text{ }^\circ\text{C}$. Cyclic voltammetry (CV) tests of the bare and coated samples were conducted in the voltage range of 2.8–4.3 V with a scan rate of 0.1 mV s^{-1} .

Electrochemical impedance spectroscopy (EIS) was measured in the frequency range from 10^5 to 10^{-2} Hz with an amplitude of 5 mV (CHI660E, Shanghai, China). Before EIS measurements, the cells were equilibrated at the charge state of 4.25 V after three cycles (0.1 C/0.1 C).

3. Results and discussion

3.1. Synthesis of the interstitial coated high nickel cathode (NCA-NCM)

The schematic illustration in Fig. 1a shows the fabrication process for the interstitial coating on $\text{LiNi}_{0.815}\text{Co}_{0.15}\text{Al}_{0.035}\text{O}_2$ with $\text{LiNi}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333}\text{O}_2$ layer (the coated materials abbreviated as NCA-NCM). The interstitial coating treatment was started with cobalt, manganese and nickel acetate completely dissolved in solvent, and percolated along the grain boundaries into the secondary particles. Then, the coating precursor gradually deposited on the surface and inside the particle because of acetates hydrolysis and solvent evaporation [14]. The modification method is simple and facile, which can be easily scale up and used for practical application.

Fig. 1b–j illustrate the morphology change of the NCA-NCM secondary particles during the coating process. Before coating, the NCA sample has a smooth outer surface on the particle (Fig. 1b), and round shaped grains inside the particle (Fig. 1c). Thereafter, plenty of nanoparticles can be observed on the surface of NCA grains after being coated with $\text{Ni}_{0.333}\text{Co}_{0.333}\text{Mn}_{0.333}(\text{OH})_2$. The surface roughness of the prepared NCA-NCM decreases significantly after annealing, indicating that the NCM333 nanoparticles were fused with the NCA grains. Unlike surface metal oxides coating in other works [1,14,15], calcination at high temperature of $780 \text{ }^\circ\text{C}$ in our work without additional lithium salt can still form an R-3m phase NCM333 coating layer with no capacity loss.

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