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Insights into the inner structure of high-nickel agglomerate as high-performance lithium-ion cathodes

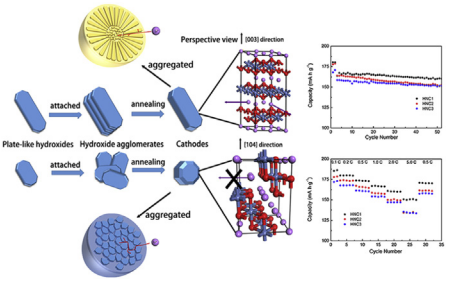
Cheng-Kai Yang [a, 1], Li-Ya Qi [a, 1], Zicheng Zuo [b], Ru-Na Wang [b], Meng Ye [c], Jing Lu [c], Heng-Hui Zhou [a, *]

[a] College of Chemistry and Molecular Engineering, Peking University, Beijing, China
[b] Beijing Engineering Research Center of Power Lithium-ion Battery, Beijing, China
[c] School of Physics, Peking University, Beijing, China

HIGHLIGHTS

- The inner structure of HNC agglomerates is systematically investigated.
- Cathodes can inherit the structure features of NCM622 precursors.
- Ordered inner arrangement offers favorable Li^+ paths and reduces cation mixing.
- HNC1 agglomerates exhibit superior electrochemical performances.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the intrinsic impact of inner structure features on the electrochemical performances of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathodes is for the first time systematically investigated. Three different spherical $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ precursors are successfully synthesized by controlling pH values and ammonia concentrations. Interestingly, via a further lithiation process, the final cathodes can gradually inherit the structural features, showing distinct particle arrangement and genetic orientation characteristics in the inner structures. Such a hereditary property can be well reined for customizing the grain-orientation, helping the growth of the inert crystal direction, reducing cation mixing and exposing the high active (100) or (010) lattice planes for lithiation/delithiation processes via an intrinsical way. The degree of grain-orientation of the primary particles turns out to be a critical factor in determining the long-term stability and power performances. Due to the reduced cation mixing degree and favorable lithium diffusion pathways, the ordered agglomerates with the grain growth along with [003] direction exhibit superior rate capability and good cycle stability.

1. Introduction

Faced with the ever-growing energy needs and environmental problems, lithium ion batteries (LIBs) stand out due to the high energy density and long service life. However, their prospective applications in hybrid electric vehicles (HEVs) and electric vehicles (EVs) are extremely restricted because the energy density of electrode materials cannot match with the increasing demands. Easing such situations have great expectations on developing renewable energy and energy-storage materials [1–3]. High-nickel cathode (HNC) systems are considered as one of the most promising

* Corresponding author.
E-mail address: hhzhou@pku.edu.cn (H.-H. Zhou).
[1] These authors contributed equally to this work.

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candidates to meet such requirements because of their high specific capacity and low cost. It can approach a reversible capacity up to 220 mA h g^{-1} with almost 80% reversible extraction of Li^+ in the cathode materials [4]. However, due to the similar radius of Li^+ (0.076 nm) and Ni^{2+} (0.069 nm), Li^+/Ni^{2+} ion exchange known as cation mixing, not only widely exists in the synthesis procedure but also in the cycling processes [5]. Other problems, such as structure deterioration and surface side reactions, also cause serious capacity decline and poor rate performance [6,7]. Despite the well-developed foreign ion doping and surface-coating strategies, relatively little emphasis has been put on manipulating the inner structure analysis to essentially meeting the above imperative challenges.

As far as the inner structure is concerned, both theories and experiments have shown it is a critical factor in addressing the major problems of the high-nickel cathodes. Since the structure of spherical particles, namely the secondary particles is inevitably fractured during the repetitive lithiation/delithiation process as a result of transient diffusion [8]. The uncoated inner particles will therefore directly expose to the electrolyte, causing side reactions and new formation of solid-state electrolyte interface (SEI) layers. Hence, comprehending the inner structure features of high-nickel cathodes can effectively apprehend their intrinsic influence on electrochemical performances [9]. Unfortunately, little success has been achieved on intensive understanding fundamental questions such as the preferred inner structures produced in the high-temperature calcined samples and effective methods to suppress the cation mixing and structure deterioration. Thus, it is of great significance to fundamentally understand the inner structures of HNC agglomerates.

In this study, “the inner structure of agglomerates” which refers to the arrangement of plate-like primary particles in the secondary particles [10], is for the first time systematically investigated. Three different $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ hydroxide precursors with tunable size and morphology were first synthesized by controlling pH values and ammonia concentration. Impressively, the final cathodes can gradually inherit the structural features of the precursors, showing different genetic orientation features in the inner structure. Such a hereditary property plays a key role in customizing the grain-orientation, suppressing cation mixing and exposing the high active (100) or (010) lattice planes for fast lithiation/delithiation processes. In addition, when the degree of ordered grain-orientation increases, due to the optimization of electronic/ionic transport properties within the electrode materials, the electrochemical performances can be dramatically boosted [11]. Among three samples, the well-orientated agglomerates with grain growth along with [003] direction present superior rate capability and good cycling stability. This fundamental study undoubtedly promotes us to raise awareness of relationships between the inner structure characteristics and the electrochemical behavior. Furthermore, it would pave new ways for designing new high-capacity battery cathodes and open opportunities for next-generation high-power energy storage systems.

2. Experimental

Synthesis of Materials. The spherical precursor $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ was synthesized by a modified co-precipitation method. Briefly, proper amounts of $NiSO_4$, $CoSO_4$ and $MnSO_4$ (cationic ratio of Ni:Co:Mn = 3:1:1) were added to a strongly stirred tank reactor under nitrogen atmosphere, forming 2.0 mol L^{-1} solution. 4.0 mol L^{-1} NaOH solution and 2.0 mol L^{-1} ammonia were added at the same time. For comparison, 4.0 and 6.0 mol L^{-1} ammonia were also added respectively. The corresponding pH values are controlled as 11.5, 11 and 10.5. The obtained precursor was then dried at 120 °C for 4 h in the air. After drying, the precursor and Li_2CO_3 were ball milled for 4 h. The Li/TM molar ratio was fixed at 1.05 [3,12]. The cathode material was heated to 550 °C at a rate of 5 °C/min, then to 850 °C at a rate of 10 °C/min and finally calcined at 850 °C for 10 h. For comparison, the different samples were heated to 400, 430, 470, 550, 700, 800 °C at a heating rate of 5 °C/min, respectively.

Materials Characterization. The particle size distribution was measured on a laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK) with dynamic light scattering (DLS) methods. The thermal decomposition behaviors were investigated by thermal gravimetric analysis (TGA) at a heating rate of 3 °C/min. The sample structures were identified by using powder X-ray diffraction (XRD, Cu Kα radiation, Bruker D8 Advance). The morphology and element distribution were analyzed using a 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 specific surface area and pore size distribution were evaluated by N_2 adsorption and desorption isotherms at 77 K (ASAP2020).

Electrochemical Tests. The working electrode was prepared by mixing active material (NCM, 90 wt%), carbon black conductive additive (Super P, 5 wt%), and polyvinylidenefluoride binder (PVDF, 5 wt%) dissolved in *N*-methylpyrrolidone (NMP). The slurry was then casted on aluminum foil and followed by drying at 120 °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 ($LiPF_6$) and Celgard 2400 film was used as 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 performances were performed on a LAND CT2001C (Wuhan, China) battery program-control test system between 2.8 and 4.3 V at different charge/discharge rate (1C = 160 m Ah g^{-1}) at 25 °C. 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). EIS measurements were performed at the charge state of 3.8 V after three cycles (0.1C/0.1C) [13]. The metal ion content was determined by the inductively coupled plasma atomic emission spectrometry (ICP-AES).

First Principle Calculation. Since the layered cathode has a similar space group with α-$NaFeO_2$ structure, the layered $LiMO_2$ model is selected to replace $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ to reduce the calculation [14,15]. Surface energies of various faces of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$, i.e. $E_{(003)}$, $E_{(104)}$ were calculated using CASTEP software package [16] based on density functional theory (DFT) within generalized-gradient-approximation (GGA). The electronic wave functions were expanded in a plane wave basis set with an energy cutoff of 500 eV. The generalized gradient approximation + U formalism developed by Dudarev et al. [17] was employed for the 3d electrons of each transition metal cation species (the U values of Ni were 5.2 eV) [18,19]. The calculation model was showed in Fig. 3 with a vacuum layer of 1.5 nm thick, which are established with the virtual crystal method [20]. The final morphology of the single crystal is determined by the model when the lowest total surface energy of the crystal is reached. The surface energy can be obtained using Eq. (1) as follows:

$$E_{hkl} = (E_{slab} - E_{bulk})/2A \quad (1)$$

where E_{hkl} is the surface energy of plane (*hkl*); E_{slab} represents the surface energy per repeating unit; E_{bulk} is the bulk atom energy; and A is the area of the related crystal planes. Number 2 in this formula means when the bonds between two nearest crystal planes