An Ostwald ripening route towards Ni-rich layered cathode material with cobalt-rich surface for lithium ion battery

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ABSTRACT An Ostwald ripening-based route is proposed to prepare Ni-rich layered cathodes with Co-rich surface for lithium-ion batteries (LIBs). Commercially available $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ and spray pyrolysis derived porous Co_3O_4 are used as mixed precursors. During the lithiation reaction process under high-temperature, the porous Co_3O_4 microspheres scatter primary particles and spontaneously redeposit on the surface of Ni-rich spheres according to Ostwald ripening mechanism, forming the Ni-rich materials with Co-rich outer layers. When evaluated as cathode for LIBs, the resultant material shows ability to inhibit the cation disorder, relieves the phase transition from H2 to H3 and diminishes side reactions between the electrolyte and Ni-rich cathode material. As a result, the obtained material with Co-rich outer layers exhibits much more improved cycle and rate performance than the material without Co-rich outer layers. Particularly, NCM-Co-1 (molar ratio of $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2/\text{Co}_3\text{O}_4$ is 60:1) delivers a reversible capacity of $159.2 \text{ mA h g}^{-1}$ with 90.5% capacity retention after 200 cycles at 1 C. This strategy provides a general and efficient way to produce gradient substances and to address the surface problems of Ni-rich cathode materials.

Keywords: nickel-rich layered cathode, cobalt-rich surface, Co_3O_4 , ostwald ripening, lithium ion batteries

INTRODUCTION

Energy crisis and environmental contamination have become increasingly serious accompanying economic boom in recent years [1,2]. New energy vehicle has been becoming more and more popular with rapid development and government support [3,4]. As one of the main energy resources, lithium ion battery has many ad-

vantages such as high energy density and long cycle life [5–19]. With the higher cruising range demands of vehicles, Ni-based lithium transition metal oxide cathode materials with high energy density have become one of the currently significant research hotspots [20–23]. Ni-based cathode materials are capable of delivering capacity over 200 mA h g^{-1} and energy density of 800 W h kg^{-1} [24]. Unfortunately, the nickel-rich surface exacerbates moisture uptake and the side reactions with electrolyte, resulting in many problems such as gelation of the cathode slurry, capacity fade, structure deterioration and thermal instability [24–27]. In addition, these nickel-rich cathodes suffer from gradual capacity fading with cycling due to their structural instability, which is ascribed to the successive phase transitions from hexagonal 2 (H2) to hexagonal 3 (H3) phases when large amounts of Li^+ are extracted from the host structure [28–33]. To solve these problems, various approaches including structure tuning [34–36], substitution [37–39], and surface coating [40–45] have been proposed. Metal oxides such as Al_2O_3 [46,47], ZrO_2 [48], MgO [49], have been studied as coating materials. The metal oxide layer is beneficial to protecting the cathode materials from being exposed to electrolyte directly, and thus reducing the side reactions. Nonetheless, the above-mentioned electrochemically inactive layer causes lower capacity and Li^+ diffusion. Therefore, electron conducting materials such as carbon and graphene [50], lithium ion conductors such as $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ [51], Li_3VO_4 [42] and Li_2ZrO_3 [52,53], have been developed as coating materials for Ni-based cathode materials. Some lithium based materials have also been used to react with residual impurities on the surface of Ni-rich cathode materials and form a uniform coating

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layer on the bulk surface at the same time [54–56]. In addition, Co-shell and concentration-gradient Ni-rich cathodes have been designed to improve the cycle life, structural and thermal stability of the Ni-rich cathodes [46,57–60]. Sun's group first reported a novel high-capacity and safe cathode material with an average composition of $\text{Li}[\text{Ni}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18}]\text{O}_2$, in which each particle consists of bulk material surrounded by a concentration-gradient outer layer [59]. However, many above-mentioned approaches are complicated and the reaction conditions need controlling strictly. An effective, easily controlled and versatile synthesis method should be constructed for Ni-rich cathodes modification.

Ostwald ripening is an typical and general phenomenon in solid solutions or liquid sols which describes the change of an inhomogeneous structure over time [61]. In our previous researches, porous Ni-Co-Mn-O powders are successfully prepared *via* spray pyrolysis [62–64]. The porous Ni-Co-Mn-O powders are composed of numerous closely packed primary particles, which would turn to submicron-sized particles after solid-state reaction with lithium salt. It seems that the binding force between the adjacent primary particles is too weak to withstand the reactivity. Based on the findings and Ostwald ripening theory, we propose a novel method to prepare Ni-rich layered cathodes with Co-rich surface. First, the porous Co_3O_4 microspheres are prepared from the solution of cobalt chloride *via* spray pyrolysis. Then the Co_3O_4 was mixed with $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ precursor powders and LiOH, followed by annealing in O_2 to yield Ni-rich cathode with Co-rich surface. Such Co-rich surface is expected to prevent side reactions from moisture in air and electrolyte, and to improve the structure stability by suppressing successive phase transitions from H2 to H3 phases to some extent.

EXPERIMENTAL SECTION

Synthesis and characterization

Synthesis of Co_3O_4 microspheres

The Co_3O_4 microspheres were prepared by spray pyrolysis in our previous paper [64]. The precursor solution was prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in distilled water. The concentration of cobalt chloride was 0.5 mol L^{-1} . The precursor solution was aerosolized using a 1.75 MHz ultrasonic nebulizer. The droplets stream was carried into a 3-zone vertical furnace reactor by O_2 with a flow rate of 2 L min^{-1} . The spray pyrolysis temperature was maintained at 750°C . The resulting powders were collected at

the reactor exit.

Synthesis of Ni-rich layered cathodes with Co-rich surface
Commercially available $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ as the precursor powder was mixed with Co_3O_4 in a molar ratio of 60:1 and 30:1, respectively, and then mixed with an appropriate amount of LiOH (molar ratio of Li to transition metals was 1.05). The mixture was annealed at 780°C for 15 h in O_2 . The samples are denoted as NCM-Co-1 and NCM-Co-2, respectively. For comparison, the pristine Ni-rich cathode material (NCM) was also prepared with the same process without the addition of Co_3O_4 .

The as-prepared cathode powders were characterized by X-ray diffraction (XRD, Rint-2000, Rigaku). Particle morphology was observed by a scanning electron microscope (SEM, Sirion 200). The element distributions of the samples were analyzed by energy dispersive spectroscopy (EDS) and liner scanning analyses of particle cross sections.

Electrochemical measurement

Cathode film fabrication was performed according to the procedures reported earlier [20]. The working electrode comprises 80 wt.% cathode materials, 10 wt.% acetylene black and 10 wt.% polyvinylidene fluoride (PVDF). Electrochemical performance was evaluated in CR2025-type coin cells assembled in an argon-filled glove box with both the moisture and oxygen content below 0.1 ppm. The electrolyte solution was 1 mol L^{-1} LiPF_6 in an ethylene carbonate/ethyl methyl carbonate/dimethyl carbonate solution (EC:EMC:DMC=1:1:1, v/v/v). Cyclic voltammetry (CV) was performed on a CHI 660A electrochemical workstation at a scan rate of 0.1 mV s^{-1} at room temperature. The charge/discharge tests were performed on a NEWARE BTS-51 battery tester.

RESULTS AND DISCUSSION

The formation of Ni-rich layered cathodes with Co-rich surface is schematically shown in Fig. 1. The sintering of $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ microspheres with LiOH yielded Ni-rich cathode material, while the porous Co_3O_4 scattered primary particles when it was reacted with LiOH. According to Ostwald ripening theory, small crystals dissolve and redeposit on the surface of larger crystals. Thus the molten LiOH and primary particles of Co_3O_4 deposited on the surface of $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$, and finally formed cathode material with Ni-rich core and Co-rich outer layer after lithiation reaction.

Fig. 2 shows the XRD patterns of NCM, NCM-Co-1 and NCM-Co-2, which exhibit a typical layered hex-

Figure 1 Schematic diagram for the preparation of Ni-rich layered cathodes with Co-rich surface.

Figure 2 XRD patterns and of NCM, NCM-Co-1 and NCM-Co-2.

agonal α - NaFeO_2 structure with space group $R3m$. The patterns show clear split of the (006)/(102) and (108)/(110) peaks, indicating all samples have a highly ordered hexagonal structure. The lattice parameters a , c and V are calculated based on the XRD and listed in Table 1. The lattice parameter a , c and V decrease with the increase of Co content, which is caused by smaller ionic radius of Co^{3+} (0.545 Å) compared to that of Ni^{3+} (0.56 Å). The ratio of c/a and the intensity ratio of $I_{(003)}/I_{(104)}$ are indicators for the extent of cation mixing. A higher ratio of $I_{(003)}/I_{(104)}$ indicates a lower degree of the cation mixing [65,66]. The ratios of c/a and $I_{(003)}/I_{(104)}$ increase with the

Table 1 Lattice parameters of NCM, NCM-Co-1 and NCM-Co-2

Sample	a (Å)	c (Å)	V (Å ³)	c/a	$I_{(003)}/I_{(104)}$
NCM	2.8703	14.1451	100.93	4.9281	1.68
NCM-Co-1	2.8657	14.1438	100.78	4.9355	1.72
NCM-Co-2	2.8634	14.1406	100.46	4.9384	1.81

Figure 3 SEM images of the samples: (a) Co_3O_4 ; (b) $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$; (c, d) NCM; (e, f) NCM-Co-1; (g, h) NCM-Co-2.

increase of Co content, indicating lower cation disorder for the Ni-rich layered cathode with Co-rich surface. A more superior layered structure and lower degree of the cation mixing for Ni-rich cathodes with Co-rich surface may help to improve the electrochemical performance [67,68].

The morphologies of Co_3O_4 , $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$, NCM, NCM-Co-1 and NCM-Co-2 are imaged by SEM, as shown in Fig. 3. Fig. 3a shows that Co_3O_4 microspheres are developed from numerous interconnected primary particles. Fig. 3b indicates the $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ microspheres are composed of densely aggregated and needle-shape primary particles with a diameter of 5–8 μm . After high temperature solid-state reaction with lithium salt, the as-prepared NCM particles (Fig. 3c, d)

Figure 4 EDS linear scanning analyses of particle cross sections of the samples: (a, b) NCM; (c, d) NCM-Co-1; (e, f) NCM-Co-2.

keep the homogeneous spherical morphology and particle diameter. The surface of the pristine NCM is bare and clean. While for the NCM-Co-1 (Fig. 3e, f), many rock-shaped grains (marked by yellow circles) adhere to the surfaces of the spheres to form a coating layer on the surface of NCM. Such layer is presumed as the redeposit Co-rich phase which is generated from the scattered cobalt species by Ostwald ripening. With the amount of Co_3O_4 increasing, the rock-shaped grains on the surface of NCM-Co-2 (Fig. 3g, h) increase and the outer layer becomes thicker than that of NCM-Co-1. There are also some fragmentized cobalt species distributed among the NCM-Co-1 and NCM-Co-2 samples, as indicated by the green arrows in Fig. 3e and g.

The ICP testing results indicate chemical composition of NCM, NCM-Co-1 and NCM-Co-2 is $\text{Li}_{0.998}\text{Ni}_{0.796}\text{Co}_{0.101}\text{Mn}_{0.103}\text{O}_2$, $\text{Li}_{0.997}\text{Ni}_{0.759}\text{Co}_{0.144}\text{Mn}_{0.097}\text{O}_2$ and $\text{Li}_{0.998}\text{Ni}_{0.723}\text{Co}_{0.184}\text{Mn}_{0.093}\text{O}_2$, respectively, consistent with the stoichiometric composition $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, $\text{LiNi}_{0.762}\text{Co}_{0.143}\text{Mn}_{0.095}\text{O}_2$ and $\text{LiNi}_{0.727}\text{Co}_{0.182}\text{Mn}_{0.091}\text{O}_2$. In order to estimate Co concentration at the surface of the Ni-rich microspheres, linear scanning analyses of particle cross sections were conducted by EDS (Fig. 4). For pristine NCM (Fig. 4a, b), the Co and Ni element distributions are even, and the relative elemental Ni:Co ratio across the NCM particle almost remains constant. For NCM-Co-1 (Fig. 4c, d) and NCM-Co-2 particles (Fig. 4e, f), Ni and Co have homogeneous distributions at the center of the

particle. It is noteworthy that the distributions change remarkably on the surface region of the particles, the concentration of Co decreases from the surface to the center while the Ni distribution changes in the opposite trend. These results indicate the formation of a Co-rich phase at the surface of NCM-Co-1 and NCM-Co-2.

Fig. 5 shows the electrochemical performance of NCM, NCM-Co-1 and NCM-Co-2. Fig. 5a shows the CV curves of the samples for the first cycle. In the positive sweep, NCM shows three oxidation peaks at 2.8–4.3 V, which are caused by the phase transition from hexagonal to monoclinic (H1 to M), monoclinic to hexagonal (M to H2) and hexagonal to hexagonal (H2 to H3) during the Li-ion extraction process [29–31,69]. The corresponding reversible behaviors are also clearly observed during the discharge process, and the reduction peaks are lower than the oxidation peaks because of polarization. NCM-Co-1 and NCM-Co-2 show very similar shapes and peak positions with that of NCM. The phase transition from H2 to H3 for NCM-Co-1 and NCM-Co-2 were significantly relieved, emphasizing that the Co-rich layer can improve the structure stability of Ni-rich layered cathodes.

Fig. 5b illustrates the first charge-discharge curves at 0.1 C. The as-prepared NCM, NCM-Co-1 and NCM-Co-2 deliver an initial discharge capacity of 194.1, 190.9 and 182.6 mA h g^{-1} , respectively. The discharge capacity decreases due to the lower Ni content, which is the main redox species. The corresponding initial coulombic effi-

Figure 5 Electrochemical performance of NCM, NCM-Co-1 and NCM-Co-2: (a) CV curves at the scan rate of 0.1 mV s⁻¹; (b) first cycle charge/discharge profiles at 0.1 C (c) cycling performance at 1 C between 2.8 and 4.3 V and (d) rate capability in the rate range of 0.1–5 C.

ciencies are 84.2 %, 85.8% and 86.4%, respectively. The increase of initial coulombic efficiency can be explained as follows. The pristine NCM sample shows a voltage platform from 4.2 to 4.3 V due to the phase transition of H2-H3, corresponding to the distinct redox peak at 4.23 V in the first CV curve. As a result, the sample delivers a higher initial charge capacity. This indicates that more Li⁺ ions de-intercalate from the cathodes in the first charge process, leading to the collapse of crystal structure. While for the NCM-Co-1 and NCM-Co-2 with Co-surface, the introduction of cobalt relieves the phase transition of H2-H3 to some extent, improves the structural stability, and reduces the polarization in the first charge-discharge cycle. The initial coulombic efficiency improves with the increasing of Co content. Cycle performances of the as-prepared NCM, NCM-Co-1 and NCM-Co-2 cathodes at 1 C between 2.8 and 4.3 V are presented in

Fig. 5c. NCM-Co-1 and NCM-Co-2 deliver comparatively lower initial capacities than that of NCM. After 200 cycles the as-prepared NCM, NCM-Co-1 and NCM-Co-2 deliver discharge capacities of 137.5, 159.2, and 151.8 mA h g⁻¹, corresponding to the capacity retention of 76.4%, 90.5%, and 87.7%, respectively. The rapid capacity fade of NCM can be ascribed to the successive phase transitions from H2 to H3 and the severe side reactions of the Ni-rich cathode surface with the electrolyte [68]. The Co-rich surface of Ni-rich layer cathodes can play an effective role in inhibiting the disorder of cations, enhancing the structural stability, and diminishing side reactions between the electrolyte and extremely unstable Ni⁴⁺ in highly delithiated Ni-rich cathode material. Thus, the cycling performance of NCM-Co-1 improves due to the chemical and structural stability endowed by the Co-rich surface.

Figure 6 Cycling performance of NCM, NCM-Co-1 and NCM-Co-2 at 1 C after exposing to ambient air for 2 months.

Fig. 5d shows the rate performance of the samples. Along with the increased current rates, the discharge capacities of both samples are decreased. NCM delivers higher capacity at low current rates than NCM-Co-1 and NCM-Co-2. However, NCM-Co-1 presents better rate performance than NCM, and exceeds the capacity at 5 C. The Co-rich surface plays a positive role in conductivity of lithium diffusion and improves rate performance of NCM.

Ni-rich cathode materials degrade faster than low Ni-content materials upon exposure to air due to the side reactions. To further compare the degradation of NCM, NCM-Co-1 and NCM-Co-2 during storage, the cycling and rate performance of the three samples after exposing them to air for 2 months are investigated. As shown in Fig. 6, after 100 cycles, the as-prepared NCM, NCM-Co-1 and NCM-Co-2 deliver discharge capacities of 132.9, 143.9, and 141.4 mA h g⁻¹, corresponding to the capacity retention of 75.4%, 83.2%, and 84.9%, respectively. The results confirm the Co-rich surface can prevent side reactions from moisture in ambient air, thus delay the degradation of the cathodes.

CONCLUSIONS

Ni-rich layered cathodes with Co-rich surface were successfully prepared from Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂, porous Co₃O₄ and LiOH via an Ostwald ripening-based route. The Co₃O₄ spheres were cracked and a Co-rich layer is then coated on the surface of Ni-rich materials. The modified samples displayed improved comprehensive electrochemical properties including higher capacity retention and better rate performance compared with that of the pristine one, ascribed to their lower disorder of cations, the suppression of phase transition from H2 to

H3, and the prevention of direct contact between the electrolyte and Ni-rich cathodes. On the basis of these results, such an Ostwald ripening-based route could be considered as a viable surface modification method for improving the electrochemical and thermal properties of Ni-rich layered cathodes.

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Conflict of interest The authors declare that they have no conflict of interest.

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奥斯特瓦尔德熟化法制备具有富钴表层的高镍正极材料的锂离子电池高镍正极材料

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摘要 本文提出了一种基于奥斯特瓦尔德熟化制备具有富钴表层的高镍正极材料的方法. 采用了商业化的 $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ 和喷雾热解制备了多孔 Co_3O_4 作为前驱体. 在高温固相反应锂化过程中, 多孔的 Co_3O_4 会分解成颗粒. 根据奥斯特瓦尔德熟化过程, 这些颗粒与锂盐反应并自发地沉积于高镍材料的表面, 形成具有富钴表层的高镍正极材料. 作为锂离子电池正极材料时, 改性后的材料中阳离子的混排得到抑制, H2到H3的相变程度降低, 并减少了电解液和高镍正极材料之间的副反应. 因此, 具有富钴表层的高镍正极材料相比于原始材料循环和倍率性能得到很大提升. NCM-Co-1 ($\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2/\text{Co}_3\text{O}_4$ 的摩尔比为 60:1)在1 C下循环200次放电容量仍有 $159.2 \text{ mA h g}^{-1}$, 容量保持率为90.5%. 本工作为制备梯度正极材料以及解决高镍正极材料的表面问题提供了一种通用而有效的方法.