



Hierarchical functional layers on high-capacity lithium-excess cathodes for superior lithium ion batteries



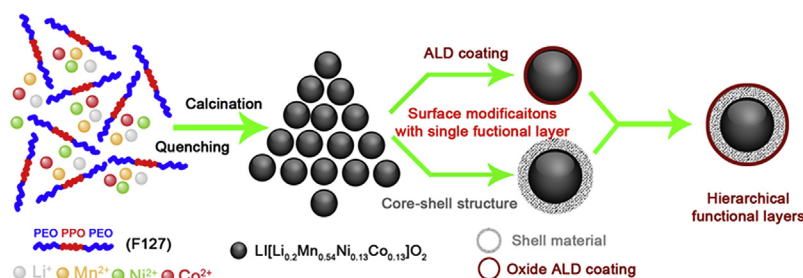
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HIGHLIGHTS

- LMNCO nanoparticles were synthesized via using surfactant-assisted dispersion.
- The effect of ALD oxide coatings on LMNCO cathode has been systematically studied.
- Li-excess LMNCO core was modified with different Li-stoichiometric shell materials.
- Hierarch functional layers on LMNCO cathode contribute to improved rate capability.
- Surface-modified Li-excess cathode delivers high capacity of 259.8 mAh g⁻¹ at 1C.

GRAPHICAL ABSTRACT



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ABSTRACT

Li-excess layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ (LMNCO) nanoparticles are facilely synthesized using a surfactant-assisted dispersion method. Ultrathin and conformal oxide coatings are deposited on the surface of individual LMNCO nanoparticle via atomic layer deposition (ALD). The effect of oxide ALD coatings on improving electrochemical performance of LMNCO electrodes is evaluated and optimized via tuning the coating thickness and composition. In addition, we synthesize a novel core-shell structure cathode consisting of Li-excess LMNCO as core and Li-stoichiometric material as shell, and its electrochemical property is optimized by tailoring weight content and composition of shell materials. Finally, electrochemical performance of Li-excess cathode material can be maximized by surface modification with hierarch functional layers composed of 10 wt.% LiCoO_2 shell (~10 nm thick) and 6ZrO_2 ALD layers (~1 nm thick), which delivers very high initial discharge capacities of 296.4, 259.8, 156.6 and 104.2 mAh g⁻¹ at 0.1C, 1C, 5C and 10C, and can retain 184.0 mAh g⁻¹ at 1C after 100 electrochemical cycles. Such remarkably improved cycleability and rate capability of nanoarchitected Li-excess layered cathode material can be attributed to the synergic effect from hierarchical functional coatings to reduce electrochemical polarization, structural degradation and side reactions during electrochemical cycling.

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1. Introduction

Rechargeable lithium ion battery has been demonstrated as an excellent electrochemical energy conservation and storage system. Tremendous research efforts have been focused on developing safe and environmentally friendly electrode materials that have high operating voltage, high energy density, excellent rate capability and

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cycling stability [1,2]. The lithium alloys as anode materials for lithium ion batteries, such as lithium–silicon (Li–Si) and lithium–tin (Li–Sn), promise to provide excellent cycling stability, high rate capability, and higher specific capacity than conventional carbon materials with a theoretic capacity of 4000 and 990 mAh g⁻¹, respectively [3,4]. On the other hand, due to limited theoretical capacity and structural instability at high voltage, the traditional Li-stoichiometric cathode materials, e.g., layered LiCoO₂, spinel LiMn₂O₄, and olivine LiFePO₄, have low reversible specific capacity up to 170 mAh g⁻¹ [5]. The development of high-performance lithium ion batteries requires breakthrough increase in the capacity of cathode materials. Recently, Li-excess layered Li[LixM_{1-x}]O₂ (M = Mn, Ni, and Co) materials have attracted much research attention due to its high theoretical capacity (>250 mAh g⁻¹) and high operating potential (>4.5 V) [6–24]. The Li-excess oxide can be considered as either a solid solution or a composite oxide consisting of Li₂MnO₃ and LiMO₂ (M = Mn, Ni, and Co), in which LiMO₂ shares the same close-packing oxygen structure from a robust Mn-based layered structure of Li₂MnO₃ [5,7,22,23]. The structural compatibility between LiMO₂ and Li₂MnO₃ as layered rock-salt structures allows for their structural integration. The high capacity of Li-excess layered cathode material has been demonstrated from electrochemical activation of inert Li₂MnO₃ at the initial charge to 4.8 V vs. Li/Li⁺. In this electrochemical activation process oxygen will be irreversibly lost together with lithium ion extraction as lithia when Li₂MnO₃ is decomposed to Li₂O and MnO₂. Hence, the oxidation state of the transition metal ions is decreased in comparison with that in the initial material at the end of the first discharge to 2.0 V vs. Li/Li⁺ [6,13,25]. The initial Li₂MnO₃ activation contributes to the high capacity of Li-excess layered cathode in the subsequent electrochemical cycles but also the low Coulombic efficiency of the first cycle. However, the easy oxidation in transition metal redox pairs during the initial Li₂MnO₃ activation induces severe decomposition of electrolyte [29]. Subsequently, phase transformation and transition metal dissolution occur in the layered structure of Li-excess cathode due to the elimination of oxygen ion vacancies via atomic rearrangements, resulting in significant irreversible capacity loss and structural instability of working electrode [17]. In spite of the high capacity, these layered cathode materials suffer from significant irreversible capacity loss in the initial charge/discharge, inferior rate capability and poor reversibility. The unfavorable cycling performance of Li-excess layered cathode materials at high charge/discharge rates can be attributed to structural rearrangement, poor electronic conductivity and severe side reactions on the cathode surface [6,7,15,19,24,25]. These factors summarized above together hinder the commercial application of Li-excess layered cathode materials.

Several approaches have been reported to solve the issues of Li-excess layered cathode materials mentioned above via metal ion doping, surface modification, preparing nanocomposite, and fabricating nano-sized materials [14,26–36]. Surface modification is extensively utilized due to its simplicity and effectiveness. A variety of surface coatings have been synthesized to ameliorate properties of underlying Li-excess cathodes, and thus improve its reversibility, rate capability and cycleability [5,37]. The coating materials can be divided into two categories: Li-active and Li-inert materials. To date, Li-inert coating materials reported in literature include metal oxides [25,28], metal fluorides [26,27], metal phosphates [26,29], carbon-based materials [24,36], and so on. Among these inert coating materials, surface modification via oxide coatings (e.g., Al₂O₃, ZnO, ZrO₂, MgO, MnO, SnO₂ and CeO₂) has been demonstrated as one of the most effective approaches to improve cycling performance of Li-excess layered cathodes [12,26,28,33]. The oxide coating not only serve as a physical protection barrier that prevents cathode from direct contact with non-aqueous

electrolyte but also as a HF scavenger that reduces acidity of electrolyte. In addition, the oxide film can act as a solid framework to restrict the disordered phase transformation, leading to better structural stability [25,38,39]. However, surface modifications with electrochemically inactive materials will decrease the energy and volumetric densities of active cathode materials and affect lithium ion and electron transfer in working electrodes [40]. Compared to thick and incomplete oxide coatings prepared by traditional wet chemical methods, films grown using atomic layer deposition (ALD) are uniform, dense, homogenous, pinhole-free, and extremely conformal to the underlying substrate, and the thickness of coatings can be precisely controlled at atomic level [41–46]. ALD is a thin film deposition subjected to a sequence of chemisorption and self-terminating surface reactions. ALD oxide coatings have been used to enhance electrochemical performance of common cathode materials, such as LiCoO₂ [41,42] and LiMn₂O₄ [43,46]. However, there are only a few reports investigating the effect of oxide ALD coatings on Li-excess layered cathode materials [25].

On the other hand, fabrication of core–shell structures via “wet-chemical” methods is a common route to introduce Li-active materials as shells on the surface of core materials [14,21,40,47–52]. The electrochemically-active shells can improve electronic conductivity, lithium ion diffusivity, thermal stability, and cycling stability of core Li-excess cathode materials. In order to improve cycling stability, X. Yang et al. employed Li-rich Li_{1.15}[Ni_{1/4}Mn_{3/4}]_{0.85}O₂ as the shell enwrapping core Li_{1.15}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.85}O₂. The as-prepared core–shell composite shows significantly enhanced cycling performance, due to better structural stability of the core–shell structure [51]. D. Kim et al. introduced spinel Li-poor Li_{0.5}Mn_{0.65}Ni_{0.35}O₂ shell on core 0.3Li₂MnO₃·0.7LiMn_{0.5}Ni_{0.5}O₂ cathode, which can decrease lithium content in the parent ‘layered–layered’ structure and enhance its electrochemical property [14]. Q. Qiao et al. have reported that coating LiMnPO₄ on the surface of Li-rich layered Li[Li_{0.17}Ni_{0.25}Mn_{0.58}]_{0.83}O₂ followed by heat treatment can increase reaction kinetics and structural stability of core material, resulting in better rate capability and cycleability in comparison with bare cathode [52]. Overall, core–shell structured composites have been designed to combine advantages from both core and shell materials for enhanced electrochemical performance.

Among solid solutions of layered cathode materials, Li [Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ in a two component notation as 0.5Li₂MnO₃·0.5LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ (hereafter marked as LMNCO) has received particular interest, due to its higher theoretical capacity of 321 mAh g⁻¹, better cycling stability and rate capability than other Li-rich analogs; thus it is an excellent candidate as cathode for applications in superior lithium ion batteries with high energy and high power [53,54]. As shown in Fig. 1, hierarchical functional layers on LMNCO cathode are designed in this work and expected to achieve a synergetic effect from ALD oxide coating and core–shell structure for superior battery performance. We first synthesize Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ nanoparticles by using surfactant-assisted dispersion. The triblock co-polymer F127 serves as the dispersant in sol–gel method. In comparison with micro-sized materials, nanomaterials offer more active sites for lithium ion insertion and extraction due to the larger surface-to-volume ratio, and provide more flexibility for volume expansion/contraction during lithiation/delithiation process, resulting in higher specific capacity and improved cycleability. Furthermore, nanomaterials provide larger electrode/electrolyte contact area and shorter lithium ion diffusion path, leading to superior rate capability. However, associated with these benefits, the high surface area and complex structure of nanomaterials will exacerbate undesirable side reactions in terms of decomposition of electrolyte and dissolution of transition metal ions [37]. In order to improve

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