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High-rate layered lithium-rich cathode nanomaterials for lithium-ion batteries synthesized with the assist of carbon spheres templates

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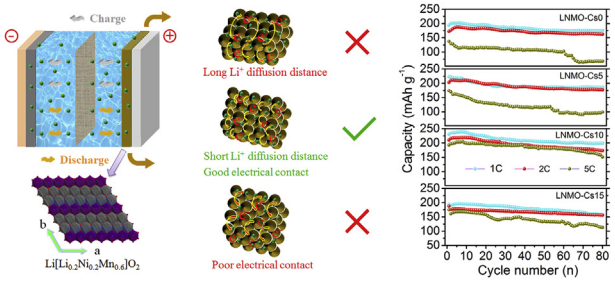
HIGHLIGHTS

- Carbon spheres were synthesized by the first hydrothermal step.
- Properly dispersive nano-Li $[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ were prepared.
- The as-prepared $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ exhibits the optimal high rate performance.
- Superior rate capability is attributed to its good dynamic characteristics.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanoparticles of the layered lithium-rich cathode, $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$, have been synthesized via the two-step hydrothermal reactions combined with calcination process, while carbon spheres were used as templates. In the first hydrothermal step, the carbon spheres templates are obtained, and then the Li $[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ materials are prepared during the second hydrothermal step with addition of 0, 5, 10, 15 wt% as-prepared carbon spheres. Structural and morphological characterizations indicate the well-ordered layer-structured lithium-rich nanomaterials can be obtained with adding proper amount of carbon spheres templates. The electrochemical test demonstrates that the sample added 10 wt% carbon spheres (LNMO-Cs10) exhibits the best performance among all the samples. It delivers the optimal cycling ability, the least voltage decay, and the maximal discharge capacities of 238.7, 219.3, 204.8 and 182.7 mAh g^{-1} at 1C, 2C, 5C and 10C rates, respectively. EIS test shows that the LNMO-Cs10 material also has the reduced solid-electrolyte-interface resistance and charge transfer resistance. The excellent cycling ability and rate capability are possibly attributed to the better dispersibility of the nanoparticles with adding adequate amount of carbon spheres templates during materials synthesis. It can both guarantee the good contact between electrode and electrolytes and prevent high aggregation of nanoparticles.

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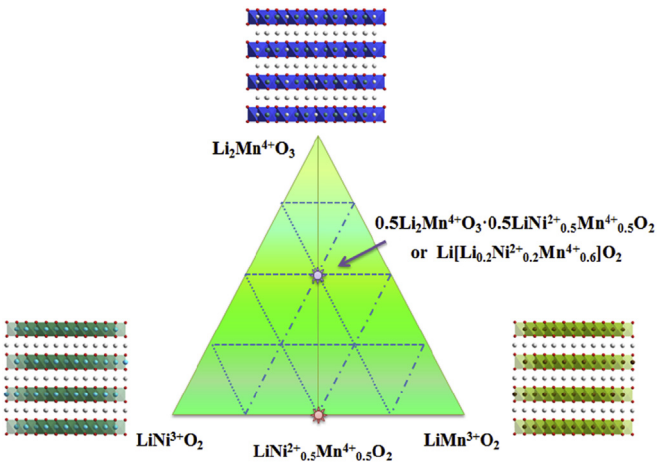
1. Introduction

Lithium-ion batteries (LIBs) have been intensively utilized as promising energy sources in portable electronics, electric vehicles (EVs), hybrid electric vehicles (HEVs) and smart grids, owing to their high energy density, long cycle life and environmental benignity [1,2]. So far, the development of the anode materials and electrolytes can roughly fulfill the requirements of LIBs, while lack of high-performance cathode materials has been considered as the bottle-neck. Stimulated by this, layered lithium-rich cathode materials $xLiMO_2 \cdot (1-x)\,Li_2MnO_3$ (M = Ni, Co, Mn, etc.), have attracted considerable attentions as promising cathodes for LIBs, since they can display high capacity of more than 250 mAh g^{-1}, high operating voltage, environmental benignity and low lost [3–10]. Currently, it is discovered that the composite $0.5LiNi_{0.5}Mn_{0.5}O_2 \cdot 0.5Li_2MnO_3$ possesses the optimal electrochemical performance in series of the layered lithium-rich composites [11–13], which is also well known as $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ shown in Scheme 1. However, although having numerous superior features, such oxides suffer from intrinsic poor rate capability and cycling ability as well as voltage fade during cycling, which is related to their relatively low ionic and electronic conductivity, as well as surface and bulk structural transformation triggered by the activation of the Li_2MnO_3 component during high voltage cycling [14–16].

To improve the electrochemical properties of these cathode materials, various strategies have been adopted, such as doping and surface modification [17–22]. But these strategies require introduction of new substances, and there are certain limitations of the species and dosage of the doping elements or coating materials as well. In consequence, it is essential to seek for other candidate ways to improve the electrochemical performance of these cathode materials. It is well acknowledged that the morphology of the particles has significant effect on the electrochemical performance of the cathode materials [23], which has been also observed in our previous reports [24–26]. Reducing the particle size to nanoscale level is one of the most efficient means to enhance materials kinetic properties [27]. However, nanoparticles have the disadvantages of poor electric contact as well as thermodynamics instability or trend to high agglomeration, possibly impeding diffusion properties of electrons or lithium ions and then dragging on the electrochemical enhancement of cathode materials. Therefore, homogenously dispersion, with a proper extent of agglomeration by the assistance of proper templates during materials synthesis, are necessary to the cathode nanoparticles, so that the contact area between the materials particles to particles and particles to electrolyte can be possibly adjusted to the optimal condition. It enables the as-prepared materials to provide more active sites and routes for electrochemical reactions with high efficient electronic transferring and ionic diffusion. Accordingly, it is beneficial for the electrons transfer and lithium ions insertion/extraction for cathode materials.

To enhance the rate capability of the $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ material, this paper proposes a rational morphological design. First, the carbon spheres (Cs), synthesized via the first hydrothermal step, were introduced as the templates to optimize the morphological characteristics of layered cathode materials, and then the binary layered lithium-rich $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ were obtained in the second hydrothermal step assisted with as-prepared carbon spheres combined with high-temperature calcination. By this, the properly dispersive nanoparticles were acquired without high-aggregations. The carbon spheres added in hydrothermal reactions are expected to be decomposed and generate a mass of gas during the subsequent high-temperature calcination process, which would be beneficial for nanoparticles dispersion in the electrode materials. It is demonstrated that particles agglomeration appears to be serious when small amount of carbon spheres is used. In contrast, the particles would be too scattered to be adverse for the electrons transferring, when excess carbon spheres are introduced. Therefore, addition of appropriate amounts of carbon spheres can possibly endow the as-prepared samples with the optimal particle aggregation, ensuring enough contact between electrode materials and electrolyte, and favorable electrical contact among particles, thus yielding superior discharge capacities, cycling ability and rate capability.



Scheme 1. Compositional phase diagram of the layered lithium transition metal oxides: $LiNiO_2$–$LiMnO_2$–Li_2MnO_3.

2. Experimental

2.1. Synthesis of carbon spheres

All chemicals used in this study are analytical grade. In this work, carbon spheres were synthesized by a hydrothermal method. Generally, a certain amount of glucose was dissolved in distilled water to form a clear solution. The aqueous solution was then transferred into a 100-mL Teflon-lined stainless steel autoclave, 60% fill, and maintained at 180 °C for several hours to obtain brownish black solution. Then, the solution was cooled down to room temperature. The products were cleaned by three cycles of filtration/washing/redispersion in water and in alcohol respectively, and subsequently oven-dried at 80 °C under vacuum overnight to gain the carbon spheres for further experiments.

2.2. Synthesis of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ materials

The binary $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ lithium-rich cathode materials were synthesized by a facile hydrothermal method assisted with carbon spheres templates combined with solid state calcination process. The concentration of the objective products was 0.3 M. Firstly, stoichiometric amounts of $Mn(CH_3COO)_2 \cdot 4H_2O$ and $Ni(CH_3COO)_2 \cdot 4H_2O$ were dissolved in distilled water. After a few minutes, 0, 5, 10 and 15 wt% carbon spheres equivalent to Li $[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ were added into the above solution under stirring, respectively. Then, stoichiometric amounts of $LiCH_3COO \cdot 2H_2O$ and oxalic acid were added separately and the solution turned to be slurry-like. The resulting slurry continued to stir for half an hour and then was transferred into a 100-mL Teflon-lined stainless steel autoclave with 60% fill. The autoclaves were then sealed and maintained at a constant temperature of 180 °C for 8 h in an oven to obtain the precursors. Then the precursors were dried, grinded, subsequently preheated at 450 °C for 3–5 h, and thereafter calcined at 900 °C for 12–15 h in air. The four samples were labeled as