



Porous layered lithium-rich oxide nanorods: Synthesis and performances as cathode of lithium ion battery



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ABSTRACT

A layered lithium-rich oxide, $\text{Li}[\text{Li}_{0.19}\text{Mn}_{0.32}\text{Co}_{0.49}]\text{O}_2$, is synthesized by introducing manganese and cobalt via oxalates co-crystallization in reverse micellar microemulsion. The physical and electrochemical performances of the as-synthesized oxide are evaluated as cathode of lithium ion battery. The physical characterizations, from X-ray diffraction, scanning electron microscope and transmission electron microscope, indicate that the as-synthesized oxide takes a nanorod morphology of up to $1\ \mu\text{m}$ in length and $200\ \text{nm}$ in diameter, which is composed of about $20\ \text{nm}$ subunit nanoparticles, and possesses a hierarchical pore structure. Electrochemical measurements demonstrate that the as-synthesized oxide exhibits improved charge/discharge performances: less polarization, larger discharge capacity, higher rate capability, and better cyclic stability, compared to the sample synthesized by introducing the transition metals in solid-state reaction.

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1. Introduction

Lithium ion battery is widely used in electronic products because of its high energy density compared to other secondary batteries [1–8]. However, the currently commercialized lithium ion battery cannot meet the requirement of energy density when used in large scale such as for electric vehicle use. Fortunately, the energy density of lithium ion battery can be improved by substituting new cathode or anode materials with larger specific capacity [2–6]. Compared to graphite anode, whose specific capacity is about $372\ \text{mA h g}^{-1}$ [9], the currently used cathode materials delivers lower specific capacity, such as LiCoO_2 ($\sim 145\ \text{mA h g}^{-1}$) [10,11], LiMn_2O_4 ($\sim 120\ \text{mA h g}^{-1}$) [7,12,13], LiFePO_4 ($\sim 140\ \text{mA h g}^{-1}$) [14–16], and $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ ($x+y+z=1$) ($\sim 160\ \text{mA h g}^{-1}$) [17,18].

Layered lithium-rich oxide $[x\text{Li}_2\text{MnO}_3 \cdot 1-x\text{LiMO}_2, \text{M} = \text{Ni}, \text{Co}, \text{Mn}, (a+b+c=1)]$ is believed to be a promising cathode material for high energy density lithium ion battery, because it could deliver a specific capacity of over $200\ \text{mA h g}^{-1}$ under a high operating potential of above $3.5\ \text{V}$ (vs Li/Li^+) [2–4,6]. However, this oxide has low electronic and ionic conductivity and thus exhibits

poor rate capability [19]. Doping and coating are the common ways to improve the rate capability of a cathode material [20–26], but these approaches are complicate and usually cause capacity loss.

Nanosized particles provide active materials with not only improved rate capability but also increased utilization because of their short distance for electron and ion transportation and large surface for charge transfer [27–31]. Therefore, much attention has been paid to the syntheses of nanosized layered lithium-rich oxide.

Three kinds of nanosized layered lithium-rich oxides have been reported, including nanoparticle or spheres (0D) [27,28], nanowire or nanorod (1D) [6,29,30] and nanodisk or nanoplate (2D) [31]. Jiang et al. synthesized hollow $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ microspheres with MnCO_3 spheres as the template, which delivered $125\ \text{mA h g}^{-1}$ at $1000\ \text{mA g}^{-1}$ [27]. Shen et al. fabricated $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ nanoparticles by co-precipitation and obtained a maximum discharge capacity of $128.3\ \text{mA h g}^{-1}$ at $1000\ \text{mA g}^{-1}$ [28]. Cho et al. used hydrothermal method to prepare $\text{Li}[\text{Ni}_{0.41}\text{Li}_{0.08}\text{Mn}_{0.51}]\text{O}_2$ nanoplates, which delivered $180\ \text{mA h g}^{-1}$ at $800\ \text{mA g}^{-1}$ [31]. They also synthesized $\text{Li}[\text{Ni}_{0.25}\text{Li}_{0.15}\text{Mn}_{0.6}]\text{O}_2$ nanowires by using hydrothermal method, which delivered $256\ \text{mA h g}^{-1}$ at $2800\ \text{mA g}^{-1}$ [29]. These reports demonstrate that the nanosized layered lithium-rich oxide with 1D structure exhibits better rate capability than those with 0D and 2D structure, which can be attributed to the continuous porous three-dimension

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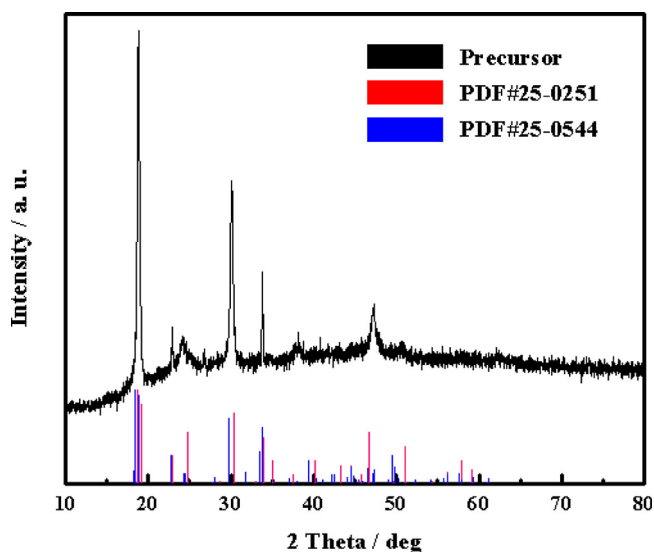


Fig. 1. XRD pattern of the precursor, co-crystallization of manganese and cobalt oxalates.

network constructed by the long wires in 1D, rather than the independent particles in 0D and compact texture of plates in 2D.

To obtain the nanowires of layered lithium-rich oxide in hydrothermal method, initial precursor $K_{0.33}MnO_2$ was first synthesized through a redox reaction between $KMnO_4$ and fumaric

acid at $700^\circ C$ for 7 h, then $Ni_{0.3}Mn_{0.7}O_2$ was obtained through ion exchange reaction of $K_{0.33}MnO_2$ in $NiCl_2$ solution for 8 days and $Li[Ni_{0.25}Li_{0.15}Mn_{0.6}]O_2$ nanowires were finally obtained through hydrothermal reaction of $Ni_{0.3}Mn_{0.7}O_2$ in $LiNO_3$ at $200^\circ C$ for 5 h [29]. Apparently, this approach is time-, chemical- and energy-consuming.

To simplify the synthesis process, reverse micellar micro-emulsion was recently adopted to obtain 1D layered lithium oxide and porous $0.2Li_2MnO_3 \cdot 0.8LiNi_{0.5}Mn_{0.5}O_2$ nanorods were successfully synthesized through the formation of MnC_2O_4 precursor in reverse micellar microemulsion and its subsequent solid-state reaction with $Ni(NO_3)_2 \cdot 6H_2O$ and $LiOH \cdot H_2O$ [6]. This product delivered $150 mA h g^{-1}$ at $2500 mA g^{-1}$. Nonetheless, the introduction of the second transition metal (nickel in this approach) in the solid-state reaction under high temperature might cause an inhomogeneous distribution of two transition metals at an atomic level and the diffusion of the introduced nickel ions into the positions of lithium ions due to the similar ionic radius of divalent nickel ion and lithium ion, resulting in the degraded electrochemical performance [32–35]. The direct evidence for the diffusion of nickel ions into the positions of lithium ions has been given by other groups, based on the observations from HAADF-STEM [32–34].

In this work, we reported a novel synthesis of 1D layered lithium-rich oxide, in which transition metals were introduced by one-step as co-crystallization of oxalates in reverse micellar microemulsion. Porous $Li[Li_{0.19}Mn_{0.32}Co_{0.49}]O_2$ nanorods were successfully obtained, which exhibited improved rate capability and cyclic stability.

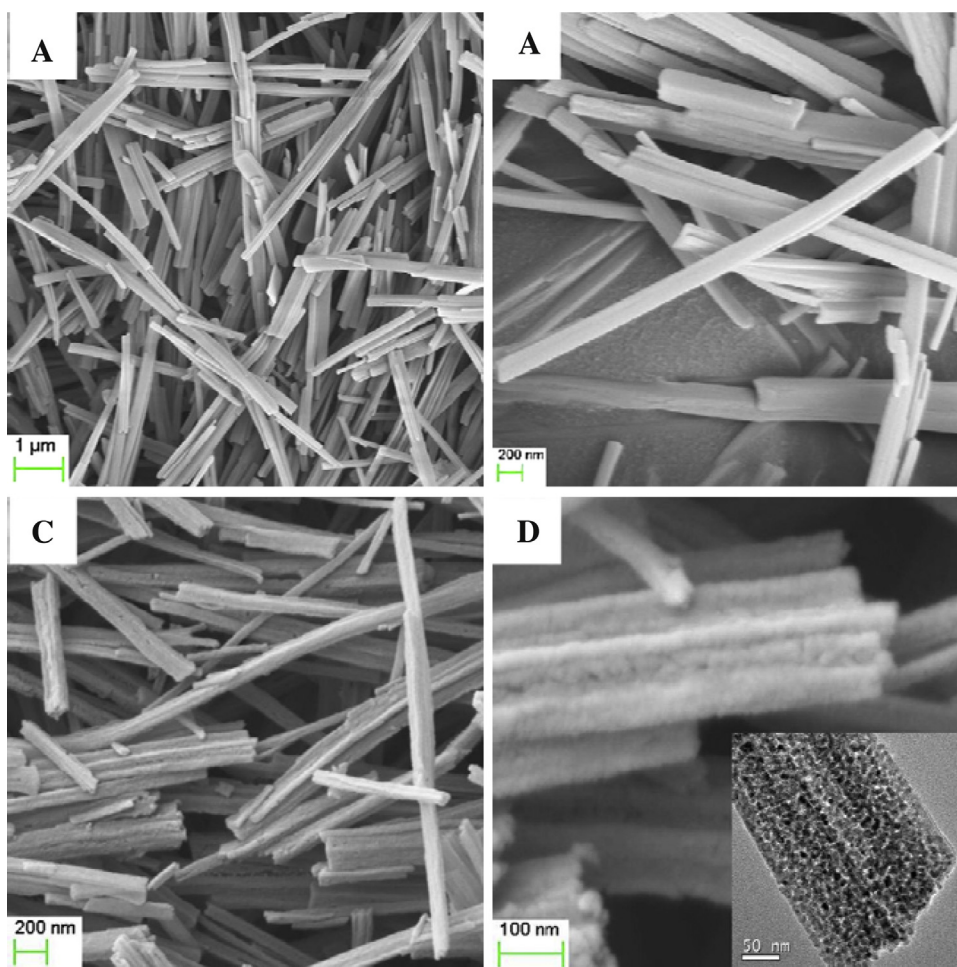


Fig. 2. SEM images of the precursors: co-crystallization of manganese and cobalt oxalates (A and B) and corresponding oxides (C and D).

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