



A design strategy of large grain lithium-rich layered oxides for lithium-ion batteries cathode



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ABSTRACT

Li-rich materials are considered the most promising for Li-ion battery cathodes, as high capacity can be achieved. However, poor cycling stability is a critical drawback that leads to poor capacity retention. Here a strategy is used to synthesize a large-grain lithium-rich layered oxides to overcome this difficulty without sacrificing rate capability. This material is designed with micron scale grain with a width of about 300 nm and length of 1–3 μm. This unique structure has a better ability to overcome stress-induced structural collapse caused by Li-ion insertion/extraction and reduce the dissolution of Mn ions, which enable a reversible and stable capacity. As a result, this cathode material delivered a highest discharge capacity of around 308 mAh g⁻¹ at a current density of 30 mA g⁻¹ with retention of 88.3% (according to the highest discharge capacity) after 100 cycles, 190 mAh g⁻¹ at a current density of 300 mA g⁻¹ and almost no capacity fading after 100 cycles. Therefore, Lithium-rich material of large-grain structure is a promising cathode candidate in Lithium-ion batteries with high capacity and high cycle stability for application. This strategy of large grain may furthermore open the door to synthesize the other complex architectures for various applications.

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1. Introduction

Environmental issues and the even-increasing oil price have spurred rapid development of electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs). Lithium-ion batteries (LIBs) have been widely used for portable electronic devices and considered as the most promising candidates to power EVs and PHEVs [1,2]. The cathode material is a key component to determine the capacity, cyclability and power/energy density of LIBs. However, conventional cathode materials, such as LiCoO₂, LiMn₂O₄, LiFePO₄ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, all deliver low discharge capacity far below 200 mAh g⁻¹, indicating that alternative positive electrode materials with higher energy density than conventional cathode materials are required to meet the design needs of future rechargeable batteries [3–7].

Recently, worldwide effort has been devoted to develop high-performance LIBs for the transportation applications, and Li-rich layered oxides with notations as xLi₂MnO₃·(1-x)LiNi_{1/3}

Co_{1/3}Mn_{1/3}O₂ have been deemed to be one of the most promising candidates for high energy cathode materials due to their high specific capacity of about 260 mAh g⁻¹ [8,9]. It has been shown that addition of extra lithium, manganese, and charge-compensating oxygen into LiMn_{1/2}Ni_{1/2}O₂ and LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ results in the formation of Li₂MnO₃-like regions or nano-domains that are structurally integrated into the LiMn_{1/2}Ni_{1/2}O₂ and LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ components [10,11]. The Li₂MnO₃ component is considered to stabilize the electrode structure and enhance the discharge capacity by extracting the lithium with a concomitant release of oxygen (i.e. a net loss of Li₂O) to form a layered MnO₂ component typically at 4.6–4.8 V [12]. However, severe surface destruction will happen due to the decomposition of electrolyte and stress-induced structural collapse caused by Li-ion [13]. Such phenomenon is common and leads to a gradual voltage drop and a steady capacity decrease during cycling which significantly restricts the application of Li-rich layered oxides as cathode materials for LIBs [14].

To improve the cyclic stability of the Li-rich layered oxides cathode materials, most of the research groups committed to modify the particle surface with metal oxides (Al₂O₃, ZnO, etc.), metal phosphate (AlPO₄), and metal fluoride (AlF₃) which can

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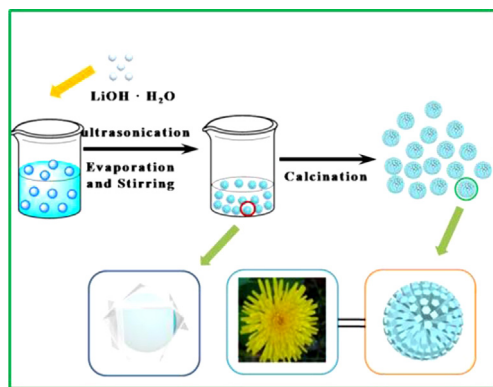


Fig. 1. Schematic illustration of the formation process of D-LMNCO.

stably exist in the electrolyte during cycling to restrict the dissolution of the surface metal ions [15–18]. However, all those efforts could merely improve the performance to a certain extent. As we all know, the crystal structure and morphology are two critical factors largely affecting the electrochemical performance of cathode materials. During the cycles, fractures of the structure and morphology are contributed to electrochemical performance decay, especially the cycling stability [19]. Due to the complicated composition, the synthesis of morphology controlled lithium-containing compounds is very difficult [20]. By means of those principles, we have designed and utilized a simple way to prepare large grain in order to improve the cycling stability of cathode materials.

In this work, we develop a simple method to synthesize daisy-like $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ (denoted as D-LMNCO) composed of large grain for the first time. D-LMNCO shows excellent electrochemical performance, including high capacity, good cyclic stability and acceptable rate performance. The overall excellent performance was achieved owing to the unique large grain, which can overcome stress-induced structural collapse caused by Li-ion and reduce the dissolution of Mn ions.

2. Experimental

The precursor for the daisy-like material was synthesized by a co-precipitation reaction. This was prepared as follows: an aqueous solution of NiSO_4 , CoSO_4 and MnSO_4 (cationic ratio of Mn:Ni:Co=0.54:0.13:0.13) with a concentration of 2 M was pumped into a continuously stirred tank reactor (flask, capacity 600 mL) under a N_2 atmosphere. At the same time, a 2 M basic solution of Na_2CO_3 was added as a chelating agent. The co-precipitation temperature was set at 60°C , and the pH value was adjusted to 8.0 by adding drops of $\text{NH}_3\cdot\text{H}_2\text{O}$, and the mixture was subsequently vigorously stirred for 24 h. Afterwards, the precursor powder was separated from the aqueous medium, followed by washing several times with water and ethanol, after which the powder was dried inside a vacuum oven at 100°C for 12 h. Thereafter, an excess amount of $\text{LiOH}\cdot\text{H}_2\text{O}$ and 2 g of the as-prepared precursor powder was dispersed into 20 mL ethanol with the assistance of ultrasound for 30 min, with the ethanol then being evaporated at 70°C whilst stirring. In this process, MCO_3 (M=Ni, Co, Mn) was uniformly covered by LiOH (denoted as $\text{MCO}_3@\text{LiOH}$). The resulting mixture was continuously ground by hand for 30 min, and then preheated at 500°C for 5 h, and finally calcined at 900°C for 12 h in air to obtain the D-LMNCO lithiated compound. This new method was called ultrasound-assisted co-precipitation method. For comparison, the spherical $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ (denoted as S-LMNCO) particles were prepared with two simple processes which are mixing $\text{LiOH}\cdot\text{H}_2\text{O}$ and the as-prepared precursor powder with the same amount of ethanol without ultrasound and using the same sintering process with D-LMNCO.

The electrode slurries were prepared by mixing the active material, carbon black (Super P) and polyvinylidene fluoride in a weight ratio of 80:10:10 together with N-methyl-2-pyrrolidone. The slurry was stirred for 3 h to ensure uniformity, and then was pasted onto an aluminum foil and dried, with a typical active material loading of about $4\text{--}5\text{ mg cm}^{-2}$. Before assembling the batteries, the prepared electrodes were dried in a vacuum oven at 100°C for 10–18 h. A half battery cell (CR2032) was assembled using the prepared positive electrode as a cathode, pure Li foil as

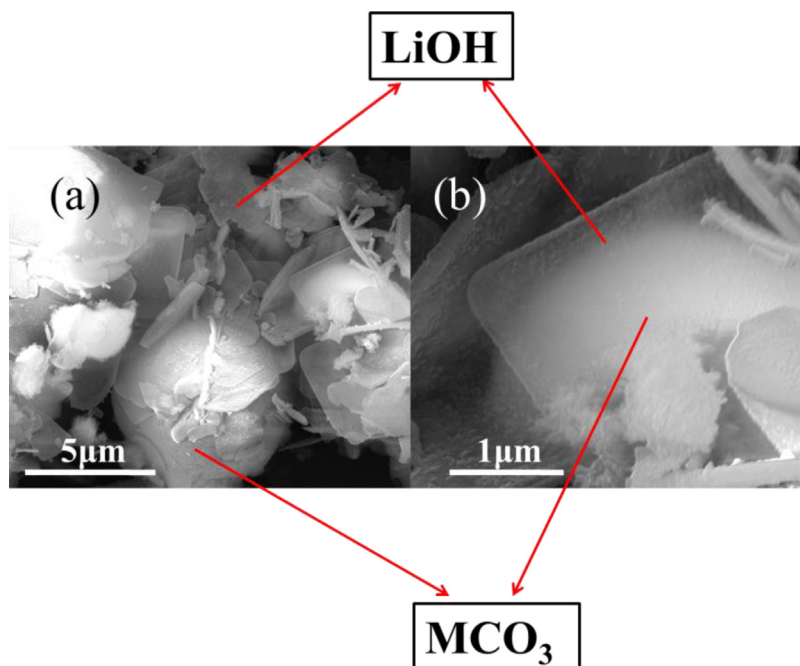


Fig. 2. (a–b) SEM images of $\text{MCO}_3@\text{LiOH}$.

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