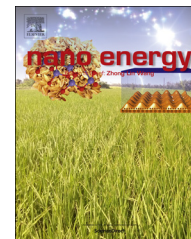




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RAPID COMMUNICATION

Synthesis of full concentration gradient cathode studied by high energy X-ray diffraction



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Abstract

Nickel-rich metal oxides have been widely pursued as promising cathode materials for high energy-density lithium-ion batteries. Nickel-rich lithium transition metal oxides can deliver a high specific capacity during cycling, but can react with non-aqueous electrolytes. In this work, we have employed a full concentration gradient (FCG) design to provide a nickel-rich core to deliver high capacity and a manganese-rich outer layer to provide enhanced stability and cycle life. *In situ* high-energy X-ray diffraction was utilized to study the structural evolution of oxides during the solid-state synthesis of FCG lithium transition metal oxide with a nominal composition of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$. We found that both the pre-heating step and the sintering temperature were critical in controlling phase separation of the transition metal oxides and minimizing the content of Li_2CO_3 and NiO , both of which deteriorate the electrochemical performance of the final material. The insights revealed in this work can also be utilized for the design of other nickel-rich high energy-density cathode materials.

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Introduction

Due to their high capacity and energy density, lithium-ion batteries are the dominant technology to power modern portable devices. The rapid development of hybrid electrical vehicles (HEVs) and electrical vehicles (EVs) creates

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urgent needs for low cost, long life, high energy-density, and safe lithium-ion chemistries to meet requirements of automobile applications [1,2]. Many cathode materials are being developed to fulfill these needs [3,4]. Lithium-rich layered-layered composite oxides and nickel-rich layered oxides have emerged as the most promising candidates for high energy-density lithium-ion batteries. The former candidate has been repeatedly demonstrated reversible capacity of up to 250 mA h g^{-1} , and with the highest gravimetric energy-density among reported cathode materials [5-8]. However, the extremely high energy-density of lithium-rich layered-layered composite cathodes can only be achieved by operating the material over a fairly wide potential window, typically between 2.0 V and 4.6 V vs. Li/Li^+ , which thermodynamically leads to a slow phase transformation of the cathode material, resulting in a continuous drop of average working potential during the normal operation of batteries using such materials [9-12]. Nickel-rich oxides are also widely pursued for their high capacity and practically accessible lithium in the oxide framework [13,14]; most of these efforts are centralized on protecting the reactive nickel-rich materials from reacting with non-aqueous electrolytes [15,16].

The nickel-rich lithium transition metal oxides are usually used to deliver a high capacity during cycling. But this compound shows a fast capacity fade and also a quick impedance rise during long term cycling [17]. Therefore, some protective layers are needed to extend their cycle life and to improve the thermal stability of these nickel-rich lithium transition metal oxides, especially at a high state of charge (SOC). These protective layers usually include electrochemically inactive metal oxides, like Al_2O_3 , ZrO_2 etc., which can extend the cycle life of the cathode to a certain degree [16,18]. While, a homogeneous coating of those oxides on cathode particles can barely be achieved using approaches other than atomic layer deposition (ALD), but the long-term stability of such ultrathin film deposited by ALD in the acidic electrolyte environment is still questionable [18,19]. In considering an approach to achieve high thermal stability and stable cycle life of nickel-rich lithium transition metal oxides [20], Sun and Amine et al. successfully demonstrated the use of a manganese-rich lithium transition metal oxide as the protective outer shell to extend the life of a nickel-rich oxide [21,22]. This strategy takes advantages of both the high capacity of nickel-rich core and the high stability of manganese-rich shell. But the drastic compositional difference between the core and the shell leads to a mismatch of their lattice parameters during charge/discharge cycling, which would eventually cause cracks inside the oxide particles [23,24].

In order to mitigate the abrupt compositional change from the core to the outer layer, the concept of a full concentration gradient (FCG) oxide was implemented by Sun and Amine et al. [25]. The FCG oxide is designed to have a nickel-rich core to deliver high capacity with a transition to a manganese-rich outer layer to stabilize the thermal stability of the oxide and also extend the cycle life of the oxide. Changing the concentration of transition metals continuously from the center to the outer edge of the oxide particles minimizes the mismatch of lattice parameters. As with other newly developed materials, significant effort is needed to optimize the synthesis condition for the best electrochemical performance [26,27]. In this work, *in situ* high-energy X-ray

diffraction (HEXRD) was used to identify key factors during solid-state synthesis that influence the electrochemical performance of the final oxide material.

Experimental section

Synthesis of FCG cathode

The precursor for FCG cathode, whose nominal composition is $\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}(\text{OH})_2$, were fabricated via a modified co-precipitation method [25]. Two nickel, cobalt and manganese metal sulfate solutions (2 M) were prepared. One is the nickel rich sulfate solution A and the other is the manganese rich sulfate solution B. The nickel rich sulfate solution A, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (Ni:Co:Mn=75:15:10 M ratio), was used as the starting materials for the co-precipitation process. During the reaction process, the manganese rich sulfate solution B, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (Ni:Co:Mn=46:23:41 M ratio), was continuously pumped into the solution A tank, which was stirred all the time to make the solution homogeneously. And then the homogeneously mixed solution is continuously pumped into a 4-liter CSTR, which was filled with distilled water and heated to 55°C . The water was purged with nitrogen while stirring at a rate of 1000 rpm. A 5-molar solution of aqueous ammonia were continuously dripped into a sealed reactor. The pH was fixed at 11.5 by adding a 10-molar aqueous solution of sodium hydroxide using a pH controller/pump. The final precursor particles were washed, filtered and dried. After each experiment, we can obtain around 200 g $\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}(\text{OH})_2$. To obtain the FCG cathode, the FCG $\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}(\text{OH})_2$ precursors are first mixed well with LiOH and then synthesized through two steps, including preheating and sintering. The first heat-treatment is called pre-heating, which heats the mixture of FCG $\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}(\text{OH})_2$ precursors and LiOH from room temperature to 500°C and held at this temperature for 10 h and then the mixture is cooled down to room temperature in the furnace. After the pre-heating, the mixture is grinded with a pestle to break any bigger particles. Thereafter, the grinded mixture is going through the second heat-treatment, sintering, which heats the mixture to a higher temperature and held at that temperature for 15 h and cooled down to room temperature in the furnace, to obtain the final FCG oxide $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$. We synthesized FCG cathode by controlling different preheating rates, different sintering temperatures and different amounts of LiOH. The detailed synthesis conditions for materials investigated here are shown in Table S1.

Ex situ high-energy X-ray diffraction (HEXRD)

The HEXRD patterns of synthesized FCG cathodes at various conditions were collected at sector 11-ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory. The wavelength of the X-ray beam used was 0.11165 \AA .

In situ HEXRD: A mixture containing FCG precursor, nominally $\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}(\text{OH})_2$, and LiOH with the molar ratio of 1:1, was grinded gently with a pestle. After grinding, the mixture was pressed into a 2 mm thick pellet with diameter of 5 mm. The pellet was then placed in a programmable furnace (Linkam TS 1500) vertically with the X-ray beam aiming at the center of the pellet. The sample was then heated from the room temperature to 950°C with a constant

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