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Effect of precursor structures on the electrochemical performance of Ni-rich $LiNi_{0.88}Co_{0.12}O_2$ cathode materials

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ABSTRACT

The structure design and synthesis of precursors is a key factor to improve the electrochemical properties of Ni-rich cathode materials. However, for the core-shell precursors, the structural evolution in the lithiated process and its effect on the structure and electrochemical properties of the final products has not been clearly elucidated. Herein, three $LiNi_{0.88}Co_{0.12}O_2$ materials are synthesized from three different structured precursors, namely the completely coated $0.88Ni(OH)_2@0.12Co(OH)_2$, the semi-coated & semi-doped $0.94Ni_{0.936}Co_{0.064}(OH)_2@0.06Co(OH)_2$, and the completely doped $Ni_{0.88}Co_{0.12}(OH)_2$, respectively. Unexpectedly, the core-shell structures of the completely coated and semi-coated & semi-doped precursors disappears, and the radial concentration distributions of Ni and Co are almost uniform in spherical $LiNi_{0.88}Co_{0.12}O_2$ particles obtained by sintering with $LiOH{\cdot}H_2O$, no matter the precursor is coating type or doping type. Even so, the $LiNi_{0.88}Co_{0.12}O_2$ material synthesized from the $0.88Ni(OH)_2@0.12Co(OH)_2$ precursor still has the best electrochemical properties with the specific discharge capacity of 215 mAh g^{-1} at 0.1 C (20 mA g^{-1}) and the capacity retention of 88.6% after 100 cycles. The reason is that the cobalt hydroxide coating layer on the surface of precursor acts as a barrier to decrease the diffusing rate of lithium ions into the core material, which leaves enough time to make Ni^{2+} be oxidized to Ni^{3+} as many as possible. This work not only synthesizes a high-performance $LiNi_{0.88}Co_{0.12}O_2$ material, but also clearly reveals the reaction mechanism and provides valuable references for synthesizing high-performance $LiNi_{1\text{-}x\text{-}y}Co_xMn_yO_2$ (NCM) or $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) materials.

1. Introduction

Because of their high energy density, rechargeable lithium-ion batteries (LIBs) have been widely used in portable electronic devices and large-scale energy storage system to resolve the intermittent power supply of renewable energy sources [1–3]. LIBs have also emerged as the most promising batteries for electric vehicles (EVs). Although LIBs-driven EVs are currently available, widespread use of electromobility still remains elusive mostly due to the limitation of the LIBs' technology. The most important technical challenges facing the current state-of-the-art LIBs for EVs are the cost, durability, and driving range, which are strongly dependent on the cathode performance [4,5]. Currently, LIBs with Li-Ni-Co-Mn-O_2 materials (for example, NCM111, NCM523) as the positive electrodes are widely used in electric passenger cars due to their high energy density [3,6–8]. Even so, the driving range of EVs (150–400 km) is still far inferior to the traditional cars driven by the internal combustion engine (500–700 km) [9]. In order to further enhance the energy density of LIBs, numerous researchers have tried to increase the Ni content to synthesize $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811), $LiNi_{0.8}Co_{0.1}Al_{0.05}O_2$ (NCA), or higher Ni content $LiNi_{0.95}Co_{0.025}Mn_{0.025}O_2$ material, thus, not only can be the driving range increased, but also the cost can be decreased [9–11]. Contrast with $LiNiO_2$, the synthesizing difficulty of Ni-rich materials ($LiNi_{1-x}M_xO_2$, M = Co, Mn, or Co + Mn) is greatly decreased, but many problems similar with $LiNiO_2$ are still not solved. On the one hand, the tendency for formation of antisite defects derives from occupation of Ni^{2+} in the lithium sites, which hinders Li^+ diffusion and decreases the overall cell performance [12–16]. On the other hand, Ni^{4+} formed under the charge process tends to react with the organic electrolyte aggressively and yields undesirable side reaction products; these reactions are aggravated particularly at elevated temperature or higher operating voltages (>4.3 V *vs.* Li^+/Li) [17]. A NiO rock-salt phase has been identified via transmission electron microscopy after several cycles at the outermost region of a grain because of the chemical instability of

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the highly oxidized Ni^{4+} [18,19]. Both the undesirable side reactions with electrolyte and rock-salt phase formation degrade the diffusion kinetics of Li^{+} during cycling, resulting in capacity fade [20,21].

Numerous attempts to improve the performance of Ni-rich materials have been mostly focused on substituting some other metal ions for Ni and coating inert inorganic materials on their surface [22]. The doping ions, such as Co, Mn, Mg, Al, etc., can effectively stabilize the layered structure and suppress Li^{+}/Ni^{2+} cation disorder [22–26]. On the other hand, through the dry coating technique or non-aqueous solvent coating technique, coating inert materials, such as Al_2O_3, AlF_3, $AlPO_4$, ZrO_2, SiO_2, V_2O_5, etc., can suppress the side reactions between the active materials and the electrolyte [27–32]. Both of the above modification techniques can to some extent enhance the cycling performance, but the specific discharge capacity also decreases at the same time.

From 2005, novel structure designs of Ni-rich $LiNi_{1-x}M_xO_2$, such as core-shell, concentration-gradient, and full concentration-gradient structures have also been developed to improve the cycling performance without compromising on the specific discharge capacity [33–35]. For example, Y. K. Sun synthesized a core-shell structured Li $[(Ni_{0.8}Co_{0.1}Mn_{0.1})_{0.8}(Ni_{0.5}Mn_{0.5})_{0.2}]O_2$ material, in which $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ acts as the core and $LiNi_{0.5}Mn_{0.5}O_2$ as the shell. This material delivers a high discharge capacity of about 188 mAh g^{-1} and excellent capacity retention of 98% after 500 cycles [33]. However, owing to the structural mismatch and the difference in volume change between the core material and the shell material, a large void forms at the core/shell interface after long-term cycling, leading to a sudden drop in capacity [36]. Thereafter, the Ni-rich materials with concentration-gradient and full concentration-gradient structures have been successively developed to solve the above problems. For example, the $LiNi_{0.83}Co_{0.07}Mn_{0.10}O_2$ with concentration-gradient structure and the $LiNi_{0.75}Co_{0.10}Mn_{0.15}O_2$ with full concentration-gradient structure have high discharge capacity and excellent cycling performance [37–40]. However, some researchers also point out that it is inevitable for the Ni^{3+}/Co^{3+}, Ni^{3+}/Mn^{4+}, and Co^{3+}/Mn^{4+} couples to diffuse into each other in the high-temperature heat-treatment [41,42]. J. R. Dahn ever reported that at 900 °C, Ni^{3+}/Co^{3+} has the highest interdiffusivity of ~4.7×10^{-12} $cm^2\ s^{-1}$, while Ni^{3+}/Mn^{4+} has the lowest of ~0.1×10^{-12} $cm^2\ s^{-1}$ [43]. Obviously, there is still much controversy on whether the core-shell or concentration-gradient structures of precursors can be maintained or not in the final products. Therefore, it is very meaningful to figure out the changing regularity of precursor structures in the reaction process and its effect on the electrochemical performance of the final materials. Ni-rich $LiNi_{1-x}Co_xO_2$ binary materials have been studied earlier, and they are still an indispensable type in Ni-rich cathode materials due to their unique properties [44,45]. Besides, compared

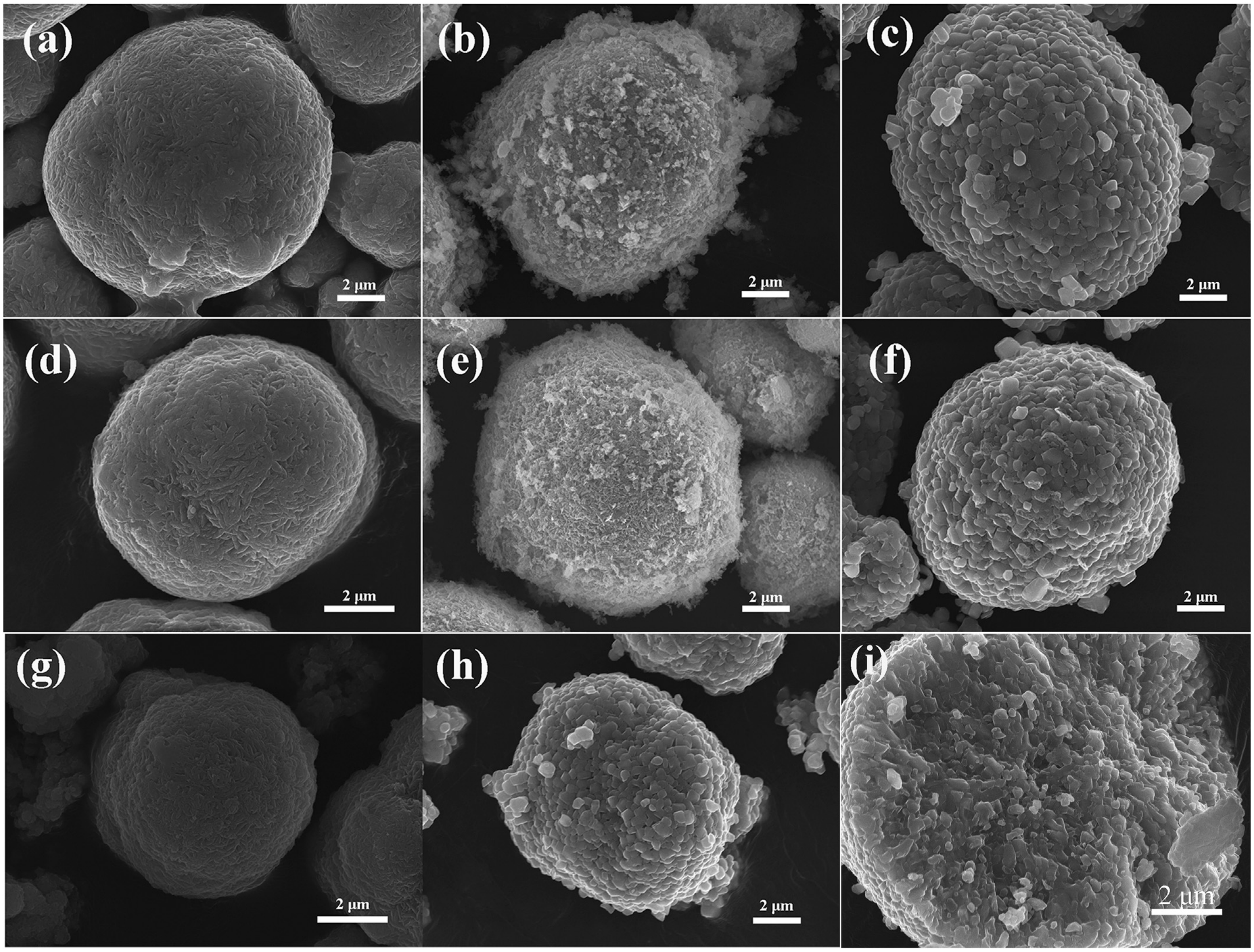

Fig. 1. SEM images of (a) $Ni(OH)_2$, (b) CC-structured $0.88Ni(OH)_2@0.12Co(OH)_2$, (c) CC-LNCO, (d) $Ni_{0.936}Co_{0.064}(OH)_2$, (e) SCSD-structured $0.94Ni_{0.936}Co_{0.064}(OH)_2@0.06Co(OH)_2$, (f) SCSD-LNCO, (g) CD-structured $Ni_{0.88}Co_{0.12}(OH)_2$, (h) CD-LNCO. (i) Cross-section SEM image of $LiNi_{0.88}Co_{0.12}O_2$ particle synthesized from the CC-structured precursor.