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Compositional core-shell design by nickel leaching on the surface of Ni-rich cathode materials for advanced high-energy and safe rechargeable batteries

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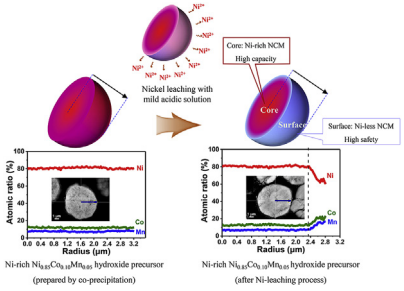
HIGHLIGHTS

- NCM hydroxide with a core-shell composition is achieved by simple acid treatment.
- Acid treatment leads to the partial Ni dissolution on the surface of NCM hydroxide.
- The Ni-less surface layer results in stable cyclability and structural stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Ni-rich layered oxides are promising cathode candidates for Li-ion batteries because of their high discharge capacity, high energy density, and low cost. However, poor cycling stability and thermal instability during cycling limit their commercial application in electric vehicles. To overcome these drawbacks, Ni-rich transition metal hydroxide precursors comprising a Ni-rich core and Ni-less surface region are successfully prepared in this study by a simple treatment process with dilute sulfuric acid. The final cathode materials have a compositional core-shell design, taking advantage of the stable cyclability and high thermal stability of the Ni-less surface layer as well as the high capacity of the Ni-rich core. The cycling stability of this Ni-rich cathode significantly improves after leaching, showing a capacity retention of 82.3% after 150 cycles at a rate of 0.5C and elevated temperature of 60 °C, much higher than that of a pristine Ni-rich cathode (65.4%). Furthermore, the thermal stability of the prepared Ni-rich cathode improves remarkably after leaching. These results suggest that the prepared cathode meets the energy storage demands of electric vehicles in terms of energy density, power, and cycling life; therefore, it is a promising cathode material for electric vehicle applications.

1. Introduction

Since their introduction by Sony in 1991, rechargeable lithium-ion batteries (LIBs) have become a common power source for portable electronic devices due to their long lifetime and high energy and power density [1–9]. More recently, LIBs have been considered to be the most promising energy storage devices for electric vehicles (EVs) and have been used for manufacturing EVs by Nissan (Leaf) and Tesla [6–19].

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Despite their environmental advantages, EVs have limited popularity because of the inferior battery performance and higher cost compared to internal combustion engine vehicles. For EVs to successfully penetrate the mass consumer market, batteries having high energy density, long life, good safety, and low price are needed [6–19]. In this regard, EV batteries require cathode materials with high energy density to achieve these properties because the most commonly used anode, graphite, can deliver a much higher specific capacity (372 mA h g^{-1}) than available cathodes.

Among the various cathode materials, layered mixed transition metal oxides such as the $LiNi_xCo_yMn_zO_2$ series, which combine the remarkable features of $LiNiO_2$, $LiCoO_2$, and $LiMnO_2$, have recently attracted more attention owing to their higher capacity, lower cost, and better cycling stability than commercial $LiCoO_2$ cathodes [1,2,4,6,8,9,13,14,16,17,20–24]. These three transition metals of $LiNi_xCo_yMn_zO_2$ cathode materials play different roles in terms of crystal structure and electrochemical properties. Generally, Ni provides the majority of the reversible capacity, whereas Co offers good electronic conductivity and reinforces the layered ordering with improved rate capability and additional capacity derived from the $Co^{3+/4+}$ redox reaction [8,16,17]. Further, Mn stabilizes the local structure to achieve a steady cycling performance, although Mn remains electrochemically inert in the tetravalent state during the charge-discharge process [8,16,17]. Consequently, the intrinsic structure and performance of $LiNi_xCo_yMn_zO_2$ strongly rely on the compositional ratio of Ni, Co, and Mn [8,9,16,17]. $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, which was first proposed by Ohzuku et al., in 2001, has been extensively studied because its practical capacity is about 160 mA h g^{-1} with acceptable rate capability characteristics [3,8,16,24–26]. Recently, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-based cathodes have been commercialized for automobile applications due to their high capacity and tolerable safety characteristics; however, it is still unsatisfactory to meet the high capacity requirements of next-generation and future EVs. Therefore, Ni-rich $Ni_{0.85}Co_{0.10}Mn_{0.05}$ (NCM) cathodes, containing more Ni content and less Co and Mn contents in the layered structure to increase the capacity concerning the $Ni^{2+/4+}$ redox couple reaction, have recently attracted widespread attention because of their high capacity within a relatively low cut-off voltage range (< 4.3 V) and their cost advantages due to lower Co content [1–17,19,20,22–24,27,28].

Unfortunately, the increase in Ni content instead of the Co or Mn content in the NCM-based layered cathode is known to directly influence the thermal stability during electrochemical reactions [1–3,5,7–13,15–17]. The highly oxidized state of Ni^{4+}, especially in the charged state, during electrochemical reactions tends to form permanent surface reconstruction layers such as spinel-like and NiO-like rock-salt phases, which subsequently cause oxygen release [2,7–9,17]. These electrochemically inactive NiO-type films strengthen the kinetic barriers against lithium ion diffusion at the interface between the electrode and the electrolyte, thus resulting in capacity fading and inferior rate capability of the cathode materials. Furthermore, the released O_2 can react with a flammable organic electrolyte, leading to massive heat and severe safety hazards, such as flames and explosions [1–3,5,7–13,15–17]. For example, a fire accident in 2016 involving a Tesla model S was caused by LIB explosions. Also, the NCM-based layered-oxide cathodes with high Ni content exhibit poorer cyclic characteristics than those with low Ni content because the residual Ni^{2+} may migrate from the transition metal layer to the Li layer in the layered structure, causing Ni^{2+}/Li^{+} mixing (cation mixing). During the charge process, Ni^{2+} in the Li layer is oxidized to smaller Ni^{3+} (0.56 Å), which deteriorates the layered structure and leads to capacity fading [2,3,8,9]. Thus, appropriate application of Ni-rich NCM materials with high capacity, long cycling life, and thermal stability is a major challenge.

Considerable effort has been made to enhance the electrochemical performance of Ni-rich cathode materials [1–3,7,10–13,15,19,22,29–33]. Among the conventional approaches, surface coating of the Ni-rich cathode materials with inorganic materials such as CeO_2, SiO_2, Al_2O_3, $AlPO_4$, and ZnO to protect the surface of the Ni-rich layered oxides in terms of structural and thermal stability has been intensively investigated [29–33]. However, the utilization of traditional inorganic oxide compounds as coating materials results in poor electronic and ionic conductivities due to the insulating characteristics of these inorganic coating layers. Although this surface modification technique typically has a positive effect on Ni-rich NCM cathode materials, the uncoated surfaces of the cathode material still cause a side-reaction with the electrolyte because of the highly oxidized state of the transition metal, especially in the fully charged state [34].

In this regard, a new material design concept based on a core-shell and/or concentration gradient structure obtained by modifying the conventional co-precipitation technique has recently been proposed to utilize the high capacity of Ni-rich NCM cathodes without degrading their structural stability, especially on the surface. A concentration gradient NCM that effectively controls the Ni composition from the surface to the bulk region by a modified co-precipitation method has been proposed to achieve high specific capacity as well as high thermal and surface stability [1,7,9,10,13,27,28]. In this co-precipitation technique for the preparation of transition metal hydroxides, the concentrations of Ni, Co, and Mn are controlled with respect to particle depth by precisely controlling the ratio of Ni, Co, and Mn during the injection of the transition metal sulfate solution for the precipitation process. This core-shell or concentration gradient structure controls the compositional ratio of the three transition metals and is attractive to design cathode materials exhibiting both high capacity and safety characteristics; however, achieving this structure requires precise experimental control during the precipitation reaction.

In this study, we report a convenient and efficient approach that effectively manages Ni composition from the surface to the bulk region of Ni-rich NCM cathodes via a simple chemical treatment. In general, all transition metals such as Ni, Mn, and Co in hydroxide precursors obtained by the conventional co-precipitation method in a highly basic environment can be completely dissolved under excess concentrated-acid solutions [35]. In contrast, under kinetically limited conditions, such as using a dilute acid solution and a short reaction time, the transition metal ions are expected to dissolve partially, in particular, on the surface of the mixed transition metal hydroxide during the chemical reaction between the hydroxide particles and the mild acid solution. Furthermore, the dissolution of Ni ions of the high-Ni-containing hydroxide particles may be more dominant during the kinetically controlled chemical reaction. Although the overall leaching rate for transition metal components can be decreased by using small amounts of acid, mild sulfuric acid has a higher probability of contacting the Ni species on the surface of the Ni-rich NCM particles. Thus, we anticipate the selective removal of Ni and consequent formation of a core-shell structure comprising a Ni-rich core region and Ni-less surface region in the Ni-rich NCM particles. This mild acid treatment of a hydroxide precursor cathode material is a facile and simple approach to achieve a Ni-less surface region exhibiting high thermal stability, while the core of the precursor hydroxide particles maintains high Ni concentrations to exhibit high capacity for practical application in LIBs.

2. Experimental section

2.1. Leaching process of Ni-rich $[Ni_{0.85}Co_{0.10}Mn_{0.05}](OH)_2$ ($NCM(OH)_2$) precursor

Commercial Ni-rich $NCM(OH)_2$ precursors (Samsung Advanced Institute of Technology, Korea) and concentrated sulfuric acid (98%, Daejung Chemical Co., Korea) were used as the starting materials for leaching. To prepare the Ni-rich $NCM(OH)_2$ precursor with a core-shell structure (Ni-less surface region and Ni-rich core region), commercial Ni-rich $NCM(OH)_2$ powders (32 mmol, based on the chemical formula of $NCM(OH)_2$) were dispersed in 100 ml deionized water, and the solution was heated to 80 °C. At this stage, various amounts of sulfuric acid (1.6, 4.8, 8, and 9.6 mmol) were added slowly into the solution, and the solution was vigorously stirred for 15 min to promote acid-