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Improving cycling performance of Li-rich layered cathode materials through combination of Al_2O_3-based surface modification and stepwise precycling

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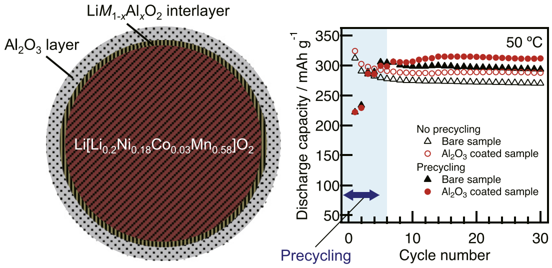
HIGHLIGHTS

- Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ was synthesized and investigated.
- The surface-modification layer is composed of Li–Al oxides and Al oxides.
- An interlayer formed between the modification layer and $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particles.
- A discharge capacity >310 mA h^{-1} and excellent cycling stability at 50 °C are achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Controlling a cathode/electrolyte interface by modifying the surface of a cathode material with metal oxides or phosphates is a concept being explored as a possible strategy for improving the electrochemical performance of such materials. This study therefore looks at the crystal structure and chemical bonding state from bulk to surface of Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ and explores the influence that surface modification has on the electrochemical performance. Investigation by X-ray diffraction, hard X-ray photoelectron spectroscopy (HAXPES) and galvanostatic charge/discharge reaction reveals that the surface-modification layer is composed of Li–Al oxides and Al oxides, with a $LiM_{1-x}Al_xO_2$ (M = transition metal) interlayer formed between the modification layer and $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particles. The cycling performance of the Li-rich layered oxide is enhanced by its surface modification with Al_2O_3, achieving a discharge capacity of more than 310 mA h^{-1} and excellent cycling stability at 50 °C when combined with a more gradual Li-insertion/de-insertion process (i.e., stepwise precycling treatment).

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1. Introduction

There is currently a demand for greater energy density in lithium secondary batteries that is being driven by their increasing use in portable energy storage devices, large-scale batteries for automobiles and power storage units. In order to meet these needs, it is essential to develop high-capacity cathode materials that are cheap, safe and exhibit good cycling performance. Recently, Li-rich layered oxides with a chemical formula of $x\text{Li}_2\text{MnO}_3-(1-x)\text{Li}M\text{O}_2$ (M = Ni, Co, Mn) have attracted considerable attention as a promising cathode material for next-generation lithium-ion batteries. These materials offer several advantages over conventional cathode materials such as LiCoO_2, including: a capacity as high as ~250 mA h g^{-1}, low cost, structural stability, and high capacity retention at high voltages [1–9]. The high capacity of these materials has been attributed to their charge/discharge reaction mechanism, which differs from conventional cathode materials in which Li^+ extraction during charging causes oxidation of the transition metal. Instead, the delithiation of Li-rich layered oxides during the initial charging process is accompanied not only by an increase in the valency of the transition metal ions, but also by the oxidation of O^{2-}. This results in irreversible oxygen loss [10,11] at the surface and/or O^- formation in the lattice [5,12,13]. Furthermore, it has been found that the specific charge reaction of Li-rich layered oxides induces a structural rearrangement [14,15], which in turn lowers the valency of some manganese ions from Mn^{4+} to Mn^{3+} [10,11,16] and results in the formation of a by-product [17] due to the oxygen-reductive reaction during the 1st discharge. Note that although Mn^{3+} in layered rock-salt-type oxides is electrochemically inactive, the structural rearrangement that occurs during the 1st charge/discharge process makes these ions active and means that the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox reaction contributes to the charge/discharge capacity from the 2nd cycle onwards. However, there is also an irreversible oxygen loss during the 1st cycle that creates microcracks at the cathode surface in conjunction with lattice distortion, thereby producing a large irreversible capacity and subsequent lowering of the cycling performance [18]. There is therefore clearly a trade-off between the activation of the manganese redox reaction after the 1st cycle and the cycling performance, which ultimately results in deterioration in crystallinity at the cathode surface due to oxygen extraction.

In previous studies, we were able to improve the cycling performance of Li-rich layered oxides, $x\text{Li}_2\text{MnO}_3-y\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2-z\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x + y + z = 1$), and increase their discharge capacity through a stepwise precycling treatment. In this, the Li^+ extraction/insertion and redox reaction of the oxide ions during charge/discharge were slowed by maintaining an upper potential limit of more than 4.5 V [18,19]. The main effect of this stepwise precycling treatment is that it inhibits the formation of microcracks at the surface of the material particles, while also preventing lattice distortion during the 1st charge to 4.8 V. Indeed, no microcracks or amorphous regions were observed in the treated samples, not even after 50 charge/discharge cycles [18].

The surface modification of cathode materials with other metal oxides or phosphates is a proven technique for preventing any loss in surface crystallinity during the charge/discharge reaction [20–26]. The main role of this surface modification layer is to protect the surface structure of the cathode material from side reactions with the electrolyte, though in the case of Li-rich layered oxides, this layer may also restrict the loss of oxygen from the lattice that would otherwise reduce the irreversible capacity of the cathode. Herein, we report a method for further improving the cycling performance of cathodes based on Li-rich layered oxides through a combination of both stepwise precycling and surface modification with Al_2O_3.

2. Experimental

Samples of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ were synthesized by mixing a Ni–Mn–Co precursor with $\text{LiOH}\cdot\text{H}_2\text{O}$. The precursor was prepared in advance through coprecipitation using $\text{Ni(NO}_3)_2\cdot6\text{H}_2\text{O}$, $\text{Co(NO}_3)_2\cdot6\text{H}_2\text{O}$ and $\text{Mn(NO}_3)_2\cdot4\text{H}_2\text{O}$ as the starting materials, and 2 mol L^{-1} Na_2CO_3 and 0.2 mol L^{-1} NH_4OH solutions as the precipitation agents. For this, the stoichiometric starting materials were first dissolved in distilled water to form a 2-mol L^{-1} solution, and then the precipitation agents were added drop-by-drop to obtain a composite carbonate precursor. This was dried at 120 °C for 5 h, sintered at 500 °C for 5 h, ground, and then mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$. This mixture was pressed into pellets, and finally sintered at 900 °C in air for 12 h. The resulting pristine $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ powder was subjected to surface modification with Al_2O_3 through a wet-coating process, in which $\text{Al(NO}_3)_3\cdot9\text{H}_2\text{O}$ was dissolved in deionized water with a pH of ~7, though this increased to ~9 following the addition of the Li-rich layered oxide powder. After being filtered, the precursor was dried at 120 °C overnight, and then sintered at 450 °C in air for 3 h.

Synchrotron X-ray diffraction patterns of the samples were obtained using the BL02B2 beam line at SPring-8, Japan. A Debye–Scherrer diffraction camera was used for the measurements, which were performed at room temperature using specimens sealed in a glass capillary (diameter: 0.2 or 0.3 mm) under vacuum. Diffraction data were collected in steps of 0.01° from 3.0° to 70°, with the wavelength of the incident beam having been calibrated in advance using a NIST SRM Ceria 640b CeO_2 standard and fixed at 0.6 Å. The lattice parameters and structures of the samples were determined by X-ray Rietveld analysis, which was performed using the RIETAN-FP program [27].

A spherical aberration (Cs)-corrected scanning tunneling electron microscope (STEM) was used to determine the distribution of Al_2O_3 on the $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ particles. Samples for this were prepared by embedding in epoxy resin to improve ease of handling, followed by mechanical grinding and Ar ion milling. A Mo grid was used as the sample holder for the Cs-STEM imaging.

High-angle annular dark-field (HAADF)-STEM imaging and energy-dispersive X-ray spectroscopy (EDX) were performed on a 2-wt%-Al_2O_3-coated $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ sample using a JEM-ARM200F system (JEOL) equipped with a “JEOL Centurio” silicon drift detector (100 mm^2) and EDX analysis station. For Cs-STEM observations, an accelerating voltage of 200 V, beam diameter of ~0.2 nm and energy resolution of ~0.5 eV (full width at half maximum (FWHM)) were used.

Hard X-ray photoelectron spectroscopy (HAXPES) measurements were performed using a VG SCIENTA R-4000 hemispherical electron-energy analyzer at the BL46XU beam line at SPring-8, Japan [28,29]. The excitation energy was set to 7939.05 eV and the analyzer was at an acceptance angle of ±7.5° from the sample. By measuring the Fermi edge of gold, the energy resolution for the HAXPES measurements was found to be ~235 meV. To inhibit peak shift attributable to the charging effect in the sample, sheet electrodes containing a conductive additive (carbon) were cut and placed on a sample stage. Using an Ar glove box, this was inserted into a transfer vessel, which was then connected to the HAXPES preparation chamber to reduce the pressure to less than 3×10^{-4} Pa. All HAXPES measurements were performed at room temperature under a pressure of less than 5×10^{-6} Pa. The escape depth was controlled by varying the take-off angle (TOA) of the