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Observation of anisotropic microstructural changes during cycling in $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material

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HIGHLIGHTS

- The microstructural changes of $LiNi_{0.5}Mn_{0.2}Co_{0.3}O_2$ during cycling are coupled with the reduction of Mn^{4+} and Co^{3+}ions.
- The anisotropic structural transformation was found in (hki0) surface regions of $LiNi_{0.5}Mn_{0.2}Co_{0.3}O_2$.
- The TEM and EELS analysis demonstrated that $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ is a promising cathode material with long cycle life.

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ABSTRACT

Microstructural changes in $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material after charge/discharge cycles were investigated by transmission electron microscopy and electron energy loss-spectroscopy. The microstructure on the surface of the cycled primary particles of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ changed from an ordered rock-salt structure into a metal monoxide-type rock-salt structure, and this was accompanied by reduction of the oxidation states of the transition metal ions, especially the Mn^{4+} ions. It should be noted that the (0001) surface of the primary particles remained intact after the cycling test. These results indicate that the degradation mechanism of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ is different from that of other $LiNiO_2$-based cathode materials previously reported. Tailoring the transition metal ion content ratios is expected to give $LiNi_{1-x-y}Co_xMn_yO_2$ various levels of surface stability.

1. Introduction

Lithium ion batteries are a promising candidate for energy storage in electric vehicles, plug-in hybrid electric vehicles, and hybrid electric vehicles. High energy density and long cycle life combined with low cost are essential requirements for these applications. Recently $LiNiO_2$-based cathode materials have been actively investigated because of their larger rechargeable capacities and lower material cost compared with conventional $LiCoO_2$ cathode material [1–5].

As the demand for $LiNiO_2$-based cathode materials with longer cycle lives has not yet been satisfied, the mechanisms of capacity fade have been investigated. The crystal structure of $LiNiO_2$-based cathode materials such as $LiNi_{1-v-w}Co_vAl_wO_2$ and $LiNi_{1-x-y}Co_xMn_yO_2$ is α-$NaFeO_2$-type ordered rock-salt structure ($R\overline{3}m$) comprising an alternating stacking of MO_2 ($M = $ Ni, Co, Mn, Al) layers and Li layers along the c axis [6,7]. Li ions can move via the two-dimensional Li layer while staying within the framework of a stacked layer structure, with subsequently reversible insertion/extraction reactions of Li ions occurring at the surface of particles. Some transition metals in the MO_2 layers have a propensity to occupy the vacant Li sites during charging and discharging. The replacement of Li ions with transition metal ions is assumed to be the main cause of capacity fade in $LiNiO_2$-based cathode materials due to decreased accommodation of Li ions [8,9]. This degraded crystal structure corresponds to a metal monoxide-type rock-salt structure.

The structural degradation of $LiNiO_2$-based materials has been closely studied by applying transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) techniques to cycled $LiNi_{1-v-w}Co_vAl_wO_2$ particles as model samples [8–12]. TEM

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analyses have revealed that the structural changes initially occur on the surface of $LiNi_{0.8}Co_{0.2}O_2$ particles [8]. A NiO-type surface layer with rock-salt structure that was 5 nm thick after the first cycle increased to 30–40 nm after cycling at 60 °C for 8 weeks. EELS analyses have shown that the local electronic states in the near-surface regions of cycled $LiNi_{0.8}Co_{0.2}O_2$ particles are different from those in the bulk [8]. The EELS profiles of the Ni-$L_{2,3}$ and Co-$L_{2,3}$ edges indicate that the oxidation states of Ni and Co in the near-surface regions are lower than those in the bulk. O–K edge profiles in the near-surface regions exhibit a significant decrease in pre-peak intensity around 528 eV, which is evidence of electronic holes in O 2p states in the bulk. These EELS results indicate that the near-surface regions of cycled particles are reductively degraded, which is consistent with the formation of a NiO-type surface layer as observed by TEM analysis.

The surface degradation mechanism appears applicable to $LiNi_{1-x-y}Co_xMn_yO_2$ systems that have the same crystal structure as $LiNi_{1-v-w}Co_vAl_wO_2$ systems. In fact, the formation of a metal monoxide-type rock-salt structure was observed on the surface of cycled particles of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ by TEM analysis [13]. However, it is unclear whether the reduction of metal ion oxidation states in $LiNi_{1-x-y}Co_xMn_yO_2$ systems is predominantly due to Ni and/or Co ions as observed in $LiNi_{1-v-w}Co_vAl_wO_2$ systems, because $LiNi_{1-x-y}Co_xMn_yO_2$ systems contain Mn ions that have a higher oxidation state than Ni and Co ions [14–17]. Hence, more information about structural transformations on the surface of $LiNi_{1-x-y}Co_xMn_yO_2$ systems is needed in order to gain new insights for designing $LiNiO_2$-based cathode materials with longer cycle lives.

In this paper, we report the results of TEM and EELS observations of the microstructure on the surface of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ particles before and after cycling. The degraded surface structure was found to have a metal monoxide-type rock-salt structure as observed in $LiNi_{1-v-w}Co_vAl_wO_2$ systems. However, two characteristic features were identified in the near-surface regions of cycled $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ particles. The first was anisotropic surface changes, and the second was reduced valence states of Mn ions. It is thought that the balance of oxidation states in Ni, Co, and Mn ions gives various levels of surface stability to $LiNi_{1-x-y}Co_xMn_yO_2$ systems.

2. Experimental

A prototype 1.5 Ah-class laminated cell was constructed using a $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$-based cathode, a $Li_4Ti_5O_{12}$-based anode, an organic electrolyte, a polyethylene separator, and a laminated film case [18]. The cathode was fabricated by coating a prepared slurry with active material, conductive additives of carbon and polyvinylidene fluoride in N-methyl-2-pyrrolidinone on the aluminum foil. The organic electrolyte consisted of a mixture of propylene carbonate (PC) and diethyl carbonate (DEC) solvent containing lithium hexafluorophosphate ($LiPF_6$). The charge and discharge cycling tests were carried out in the range of 1.5–2.7 V at a 2C (3 A) rate and 45 °C. The capacity of the cells after the first cycle and after the 4000th cycle were checked in the range of 1.5–2.7 V at a 1C (1.5 A) rate and 25 °C. The capacity retention after 4000 cycles was 80%, which is worse than previously reported because here the higher environmental temperature of 45 °C accelerated the capacity fading [18]. The cells were discharged at 1.5 V at a 1C (1.5 A) rate and then disassembled in an Ar-filled dry box. The pieces of cathode obtained from the disassembled cells were rinsed with ethyl methyl carbonate to remove the electrolyte containing lithium salts. Thin samples with the thickness of 0.05–0.1 μm for TEM and EELS observations were prepared by a focused ion beam (FIB) technique. An embedding resin was introduced into the pores of electrode not only to maintain the shape of a thin sample after the FIB process, but also to suppress artificially damaged surface layers conceivably less than 1 nm thick. The prepared samples consisted of some primary particles of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ with various crystal orientations as shown in Fig. 1. TEM observations were carried out using an FEI Tecnai Osiris operating at an accelerating voltage of 200 kV. TEM images of the zone axis perpendicular to the c axis of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ were acquired in two different types of surface regions: the $(hki0)$ $(i = -(h+k))$ surface and the (0001) surface, which are the lithium insertion/extraction interface and the basal plane of an ordered rock-salt structure, respectively. EELS data were collected using a Hitachi HD2700 operating at an accelerating voltage of 200 kV, a convergence semi angle of 28 mrad, a collection semi angle of 29 mrad and an energy dispersion of 0.36 eV/ch. The fullwidth at half-maximum of the zero loss peak was approximately 0.8 eV. The spatial resolution less than 0.5 nm is enough to observe the changes in EELS profiles collected at steps of 1 nm during a line scan.

3. Results

3.1. TEM observation of a $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ particle

Representative TEM images of the region near the $(11\bar{2}0)$ surface of a $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ particle after the first cycle are shown in Fig. 2. High-resolution TEM (HRTEM) images obtained from the boxed area in Fig. 2a exhibited a periodic lattice fringe as shown in Fig. 2b. Fig. 2c shows an enlarged view of boxed area 2 in Fig. 2b. The spacing of fringes in the bulk was estimated to be approximately 0.48 nm, corresponding to the spacing of the (0003) plane, which is the distance between two neighboring transition-metal layers along c axis. Fast Fourier transform (FFT) patterns in the bulk (Fig. 2d) were typical of an ordered rock-salt structure ($R\bar{3}m$) at the $[1\bar{1}00]$ zone axis. The spots assigned to 0003_R and 0009_R of the ordered rock-salt structure indicate a superlattice with alternating stacking of Li layers and MO_2 layers (M = Ni, Co, and Mn). The lattice fringes of the $(11\bar{2}0)$ surface region were coherent with the bulk. However, the region within a range of less than 5 nm from the $(11\bar{2}0)$ surface was distinctly different from the bulk. Fig. 2e shows

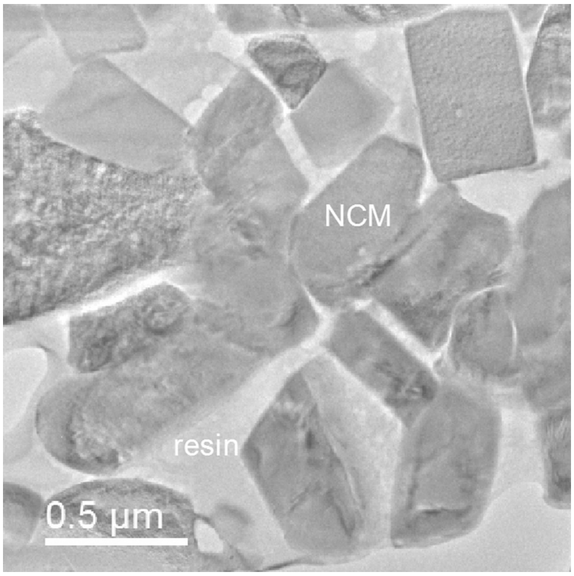

Fig. 1. Typical TEM image in a low magnification. The dark particles are $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM). The embedded resin was observed throughout the pores between particles.