Research paper

Topotactic transformation of Ni-based layered double hydroxide film to layered metal oxide and hydroxide

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A B S T R A C T

Topotactic transformation of film-shaped samples comprising a layered double hydroxide (LDH) to a metal oxide phase was performed by a hydrothermal or heat treatment. The degree of transformation was examined by X-ray photoelectron spectroscopy (XPS) and synchrotron X-ray diffraction (SXRD). The LDH film prepared as a raw material by a reflux process with urea was composed of plate-shaped particles that were partially perpendicular to the substrate. For the transformation, the LDH powder and film were treated hydrothermally at 90, 120, and 200 °C in a LiOH aqueous solution or heated to 400, 600, and 800 °C with a LiOH·H$_2$O contact. The film shape and morphology of the LDH particles were retained after the hydrothermal treatment at 120 °C. XPS and SXRD confirmed that two types of LDH with different compositions, Ni:Co = 62:38 and 90:10, were formed in the as-prepared LDH. In the case of the sample treated hydrothermally, metal hydroxide with no intercalated anion within the interlayer space was observed and the metal oxyhydroxide formed with a ratio of approximately 15%. For the heated samples, the transformation to LiNi$_{1-x}$Co$_x$O$_2$-related materials was carried out by heating to 600 or 800 °C.

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1. Introduction

Layered double hydroxide (LDH) has a layered structure with anions intercalated between brucite-type hydroxide layers. The hydroxide layer is composed of divalent and trivalent cations. The interlayer anion compensates for the charge discrepancy arising from the occurrence of trivalent cations in the hydroxide layer. Generally, the interlayer anion can be exchanged by ion-exchange or reconstruction processes. For ion exchange, Cl$^-$ or NO$_3^-$ type LDH should be used as raw materials because CO$_3^{2-}$ is generally most stable within the interlayer space. For reconstruction, calcined LDH is immersed into an anion-contained aqueous solution to rehydrate with the existed anion. The structural changes in this process have been examined by X-ray absorption fine structure (XAFS), but the formation is sometimes difficult for transition metal-containing LDH due to facile formation of a spinel-type phase (Rives, 2002). For applications of the ion-exchanged LDH, some studies have reported the preparation of functional hybrids (Pinnavaia et al., 1995; Tang et al., 2011; Takei et al., 2014), removal of toxic anions (Nakahira et al., 2007; He et al., 2011; Park et al., 2004), and use of drug delivery systems (Aisawa et al., 2006, 2007). The most common LDH is "hydrotalcite," which is composed of Mg^{2+} and Al^{3+}. For the LDH, including hydrotalcite, the divalent and trivalent cations can be replaced with period-four transition metal cations such as Cr,

Mn, Fe, Co, and Ni, because most period-four transition metals are either di- or trivalent. For the crystal structure of LDH, all metals form M(OH)$_6$ octahedra in which all OH groups are shared. For such polyhedral poly-condensation structures, six edges in an octahedron are shared with each other. The structure of the LDH is, actually, quite similar to that of LiCoO$_2$ despite the positive valence of the interlayer ion (Li$^+$). Therefore, some researchers have examined the synthesis of LiCoO$_2$-type cathode materials from LDH as a raw material (Lu et al., 2007; Yushi et al., 2008).

For LiCoO$_2$, Co occurs in a trivalent state and the Li cation can be deintercalated from the structure owing to the oxidation of trivalent Co to tetravalent Co during the charge process of a Li-ion battery. When tetravalent Co is reduced to the trivalent state, Li ions can be intercalated again. However, LiCoO$_2$ has a slight risk of decomposing with the generation of O$_2$ gas at relatively low temperatures (above 200 °C). This can be dangerous because the generation can expand the battery cell and sometimes result in an explosion. To improve the decomposition temperature, many researchers have examined some additives, partial substitution or change in composition. LiMn$_2$O$_4$ (spinel structure) and LiNiO$_2$ can decompose above 300 °C and approximately 200 °C, respectively (Biensan et al., 1999; Kitano et al., 2005). The use of LiCoO$_2$ as an electrode in secondary batteries has two disadvantages. One is the low electronic conductivity. As the conductivity of LiCoO$_2$ is approximately 10^{-3} S/cm (Kwon et al., 2014), both an adhesive agent and a conduction aid are necessary for the formation of an electrode device, particularly regarding the use of powder-type

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$LiCoO_2$. The adhesive agent and conduction aid are generally PTFE and carbon, respectively. Because $LiCoO_2$ is a p-type semiconductor, the number of holes will increase with increasing Co^{4+} concentration. Nobili et al. reported that Mg substitution at the Co site in $LiCoO_2$ results in an increase in electronic conductivity (Nobili et al., 2005). The other disadvantage is the layered structure. The structure can be an advantage because the Li cation can move within the interlayer space; however, it becomes a disadvantage for large $LiCoO_2$ particles. Large plate-like particles sometimes decelerate the intercalation and deintercalation of Li because of the long diffusion path. Because Li diffusion will be predominant, the synthesis of $LiCoO_2$ nanoparticles or the preparation of an oriented structure perpendicular to the substrate will be effective.

For these reasons, both the crystal structure and particle orientation for $LiCoO_2$-type compounds are very important. Therefore, the topotactic transformation from LDH is possible. In this study, the preparation of oriented LDH on the substrate and topotactic transformation to Ni-based layered metal oxide with a $LiCoO_2$ structure was examined by a hydrothermal and heating process. The crystal structures of the sample were examined by synchrotron-XRD (SXRD).

2. Experimental

The transformation was performed for the sample in two forms, powder and film. Both samples were prepared, which were then transformed by heating with LiOH or by a hydrothermal treatment in an aqueous LiOH solution. The typical processes are as follows.

2.1. Preparation of LDH

Ni and Co nitrate mixed salt was used as the metal sources at ratios of 1, 2, 4, and 8. Distilled water was added to the salts to achieve a concentration of 5 mmol/L. Urea was placed in the aqueous solution of the mixed salts with a molar ratio of 20. In the case of film preparation, a $10 \times 50 \times 0.2$ mm Ti or Ni plate used as a substrate was soaked perpendicular to the stirring flow in an aqueous solution. The solution was then refluxed with stirring at 120 °C for several hours. The prepared LDH are designated as mNi1Co, where m means the loaded molar ratio of Ni/Co; e.g., 4Ni1Co.

2.2. Transformation treatment of LDH powder and film

The obtained LDH underwent a transformation by a heat-treatment or hydrothermal treatment. The heat treatment was performed using $LiOH \cdot H_2O$ at 400–800 °C for 3 h in air. The $LiOH \cdot H_2O$ to metal cation ratio in LDH was 3:2. The heated samples were washed with distilled water and dried at 50 °C.

In the case of the hydrothermal treatment, the LDH samples were soaked in a LiOH aqueous solution with a concentration of 1.0 mol/L. The solution was treated hydrothermally at 90, 120, and 200 °C for 72 h. The treated samples were washed with distilled water and dried. Here, "HT" is defined as a prefix of the hydrothermal temperature for use as the sample name.

2.3. Characterization

The structure of the prepared LDH and the sample produced by the heat or hydrothermal treatments were examined X-ray diffraction (XRD) with monochromated CuKα radiation (RINT-2000, Rigaku). In the case of the film measurement, the sample film with the metal substrate was fixed on a glass slide. The surface morphology of the prepared film was observed by field emission scanning electron microscopy (FE-SEM, JSM-6500F, JEOL) with an acceleration voltage of 15 kV. The chemical states of the composed metal were examined by X-ray photoelectron spectroscopy (XPS, Kratos Axis-Ultima, Shimadzu) using monochromated AlKα radiation. For inductively couple plasma (ICP) analysis and structural refinement, the mass of the film sample

could not be obtained, which prevented accurate measurements. Therefore, the powder sample was used for these measurements. The chemical composition of the samples was measured by ICP (PS-3500DDII, Hitachi High-Tech Science Corp.) The structures were examined by SXRD using a Debye-Scherrer camera at BL02B2 in SPring-8. A borosilicate capillary tube, 0.2 mm in radius, was filled with the samples. The wavelength was 0.49560 Å, which was determined using CeO_2 as the reference crystal. The SXRD patterns were refined using RIETAN-FP (Izumi and Momma, 2007).

3. Results and discussion

3.1. Preparation of LDH film

Fig. 1 shows XRD patterns of the Ni-Co LDH powder with different compositions, Ni:Co = 1:1, 2:1, 4:1, and 8:1. The LDH phase can be observed at all compositions. However, the XRD reflection intensity increased gradually depending on the Ni ratio. Generally, because the M^{2+}/M^{3+} ratio should be 2–4, the chemical composition ranges of 2:1 and 4:1 will be the optimum because the divalent cations tend to be deficient at the higher ratio. In actual experiments, the crystallinity is high and the yield is low for 8Ni1Co. For 2Ni1Co, the yield is good but the crystallinity is somewhat low. Therefore, in this study, a 4:1 composition was adopted for the subsequent experiments.

Fig. 2 presents the XRD patterns of the grown LDH films with a Ni:Co ratio of 4:1 on the Ti substrate for different synthesis periods (1.0, 1.5, 2.0, 3.0, and 5.0 h). Their baselines appear to be worse because the substrate Ti metal is pliable and the measured surface is not flat. The halo in the sample at 1.5 and 5.0 h might be from a glass slide. These patterns suggest that the amount of LDH increases depending on the synthesis period. The patterns could not confirm whether the LDH particles were ordered or not. Fig. 3 presents the FE-SEM images of the grown LDH films with a different period, 1.0, 1.5, 2.0, 3.0, and 5.0 h. The top and bottom micrographs show the low and expanded magnifications, respectively. The LDH nuclei begin to form at 1.0 h, and the number of nuclei increases steeply during an additional 1 h. The number of LDH particles perpendicular to the substrate tends to increase over synthesis periods of 3 h or shorter. At 5 h, the particle size appears to become approximately double. However, the excess particles emerge on the perpendicular particles, as shown in the low-magnification image.

3.2. Transformation treatment for LDH

The transformation treatment for LDH was carried out by heating and/or hydrothermal treatments. Fig. 4 presents XRD patterns of the
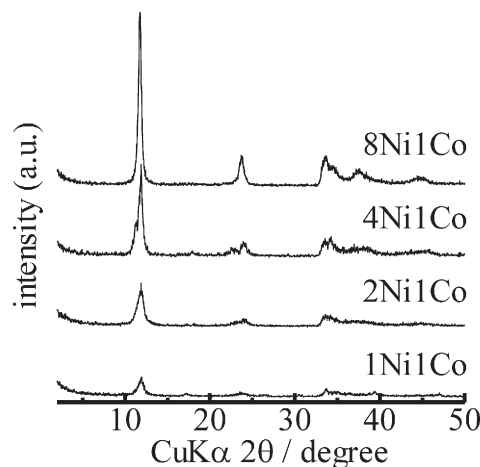

Fig. 1. XRD patterns of the mNi1Co LDH powder prepared by reflux process with urea at 120 °C with different chemical compositions (m = 1, 2, 4 and 8).