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Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Temperature-dependent structural behavior of mixed-metal hydroxides in air



Yun-Hee Lee^{a,b}, Ki-Bok Kim^{a,b}, D.H. Gregory^c, Yong-Il Kim^{a,b,*},¹

^a Korea Research Institute of Standards and Science, 267 Gajeong, Yuseong, Daejeon 305-340, Republic of Korea

^b University of Science and Technology, 217 Gajeong, Yuseong, Daejeon 305-350, Republic of Korea

^c WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland, UK

ARTICLE INFO

Article history:

Received 21 December 2014

Accepted 7 March 2015

Available online 17 March 2015

Keywords:

Mixed-metal hydroxide

Precipitation

Phase transition

X-ray diffraction

ABSTRACT

A co-precipitation process using transition metal hydrates was used to prepare a mixture of $M(OH)_2$ and $MO(OH)$ ($M = Ni_{0.5}Co_{0.2}Mn_{0.3}$). This powder consisted of dense, quasi-spherical particles each composed of plate-like particles of ca. 250 nm across. By increasing the temperature, $M(OH)_2$ was made to transform into $MO(OH)$ at ca. 220 °C, then into M_3O_4 at ca. 330 °C. Moreover, the M_3O_4 phase persisted without further reaction until 700 °C. During these phase transitions, the mixed-metal (M) in $M(OH)_2$, $MO(OH)$ and M_3O_4 retained disordered cation distributions at the same crystallographic sites of their host lattices without appearance of any phases related to Ni, Co and Mn. The $MO(OH)$ phase appeared owing to exposure to air. $M(OH)_2$ at room temperature had the lattice parameters ($a=b=2.9991(2)$ Å and $c=8.5892(2)$ Å) with space group ($P6_3/mmc$).

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1. Introduction

Recently, demand for high performance batteries with high energy storage has increased significantly. Among high-performance batteries, rechargeable lithium-ion batteries having a high-energy density and voltage, a long life-cycle and a low self-discharge rate are commercially available and widely used [1]. The three primary components of the rechargeable lithium-ion battery are the negative electrode, positive electrode, and the electrolyte. Lithium-containing cobalt oxide ($LiCoO_2$) is often used as a positive cathode for lithium-ion batteries largely due to excellent cyclic properties. This is despite being somewhat less safe, and the greater expense of Co in relation to than other transition metals such as Mn and Ni. Hence, in order to overcome these demerits, lithium-containing manganese, nickel and/or cobalt oxides (e.g. $LiMnO_2$, $LiMn_2O_4$ and $LiNiO_2$) have received a great deal of attention as cathode materials. However, they exhibit a number of deficiencies, such as a relatively low capacity, poor cycling characteristics and high production costs [2].

For these reasons, lithium-transition metal composite-oxides ($LiMO_2$, $M = Ni, Co$ and/or Mn) have been proposed as one group of

a number of emerging commercial, positive electrode materials as means by which one can maximize the individual advantages of each lithium-containing transition metal oxide in one single lithium-containing trimetallic transition metal oxide compounds [3–6].

The $LiMO_2$ compound is typically prepared by a two-step process involving metal hydroxides. The first step is a co-precipitation of a mixed-metal hydroxide ($M(OH)_2$ $M = Ni, Co$ and/or Mn) [7,8] followed in the second by calcination with the stoichiometric amount of $LiOH \cdot H_2O$ in air at a given temperature [3–6,9]. The mixed-metal hydroxide precursor undergoes a thermal treatment process from room temperature to ca. 1000 °C. Accordingly, studies on the thermal behavior of such mixed-metal hydroxides are fundamentally important to understand both the physical and chemical properties of the ensuring $LiMO_2$ compound with respect to potential applications.

Although work has been performed on the thermal decomposition of $M(OH)_2$ under atmospheric conditions, relatively little is known regarding the isothermal behavior of the compounds at given process temperature. Consequently, in this work we report on the isothermal structural behavior and the lattice constant refinement of mixed-metal hydroxides based on the analysis of powder X-ray diffraction data.

2. Experimental

The mixed-metal hydroxide powder was prepared via a co-precipitation method using manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$, 99% Sigma-Aldrich), nickel sulfate hexahydrate

* Corresponding author at: Korea Research Institute of Standards and Science, 267 Gajeong, Yuseong, Daejeon, 305-340, Republic of Korea. Tel.: +82 42 868 5448; fax: +82 42 868 5635.

E-mail address: yikim@kriss.re.kr (Y.-I. Kim).

¹ Present address: WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland, UK.

(NiSO₄ · 6H₂O, 99% Sigma-Aldrich) and cobalt sulfate heptahydrate (CoSO₄ · 7H₂O, 99% Sigma-Aldrich) as starting materials. The mixed solution was prepared by dissolving each of the reactants in distilled water. Sodium hydroxide (NaOH, 98% Sigma-Aldrich) and ammonium hydroxide (NH₄OH, 28.0–30.0% Sigma-Aldrich), as precipitating agents, were fed into the hot reaction bath (60 °C) under argon (Ar) atmosphere. The pH of the mixed solution was maintained at ca. 11.25 during the process. Pink precipitates were obtained following co-precipitation and the mixtures were stirred for 12 h under Ar atmosphere, the precipitates before filtering. The solids were washed at least five times in distilled water and dried at 100 °C for 36 h under Ar atmosphere.

Scanning electron microscopy (Quanta FEG250) using energy dispersive X-ray spectroscopy (EDS) was used to investigate the chemical composition, size and shape of the powder particles as they were synthesized. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (TA Instruments, SDT Q600) of the synthesized powder were performed using a heating rate of 10 °C min⁻¹ in air. Isothermal X-ray diffraction was performed at variable temperature using a high temperature attachment (Rigaku RINT2000) in air. Initially data was collected at room temperature, and then 10 °C increments from 50 to 700 °C. For variable temperature diffraction experiments, a range of $15^\circ \leq 2\theta \leq 100^\circ$ at a 2θ step of 0.02° was employed. Room temperature X-ray diffraction data for the synthesized powder were measured over the scattering angle range $15^\circ \leq 2\theta \leq 145^\circ$ at a 2θ step of 0.02° employing CuK α radiations with a graphite monochromator in reflection geometry (Rigaku, Dmax2200). The graphical user interface EXPGUI was used in combination with the General Structure Analysis System (GSAS) software to perform the structure refinement using the pseudo-Voigt function model the experimental peak shape [10,11].

3. Results and discussion

The as-synthesized powder was composed of dense, quasi-spherical particles with diameters within a range from ca. 2 to 14 μ m. Each particle could be regarded as a hierarchical structure composed of high density of plate-like particles ca. 250 nm across, as shown in higher-magnification SEM micrographs (Fig. 1 and inset). The plate-like particles project towards the outer surface side of the composite aggregated particles, accounting for the observed high tap density [12,13].

Standardless quantitative analysis of EDS was used to determine the average composition for the synthesized powder. The analysis is composed of a two-step process: spectrum analysis and matrix corrections. The first step is the spectrum analysis, which is used to eliminate unwanted background noise and extract the net area of spectra peaks from elements present in the sample. Second, these peak areas are used in a matrix correction algorithm to resolve any peak interferences and to determine the relationship between net peak areas for each element and their corresponding chemical concentrations. This matrix correction algorithm is essentially the final calibration for relating spectral results to elemental concentrations present in the sample. We used ZAF as a matrix correction algorithm in this study, where “Z”, “A” and “F” referring to the three parts contributors of matrix effects—the atomic number (Z), absorption (A), and fluorescence (F) [14,15]. After taking account for the matrix correction into account, the net area under the peak is converted into weight percent or atomic percent. We applied this procedure to determine the average composition of the as-synthesized powder. The result of EDS analysis performed at several points showed that the only metallic elements in the synthesized powder except were Ni, Co and Mn, as shown in Fig. 2. The mean transition metal contents

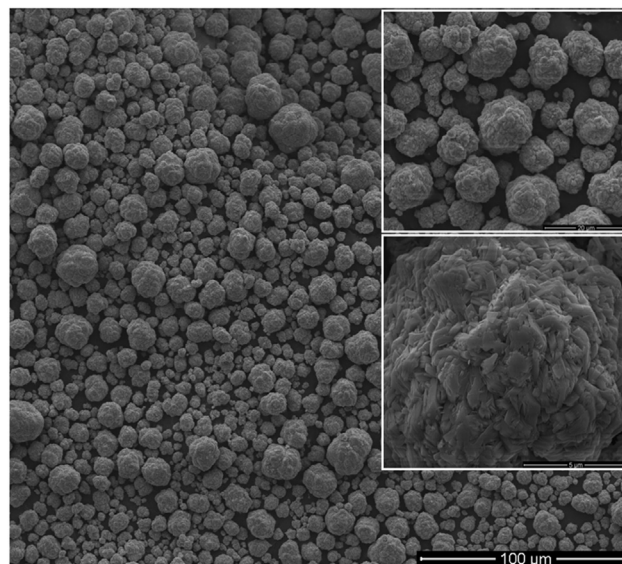


Fig. 1. SEM micrographs of the synthesized powder. The powder consisted of dense, quasi-spherical particles each composed of plate-like particles of ca. 250 nm across (inset).

based on the EDS results was 50.13 at% (at%) for Ni, 19.53 at% for Co, and 30.34 at% for Mn on the assumption that oxygen (O) and hydrogen (H) maintained stoichiometric values consistent with the formation “M(OH)₂”. Consequently, the stoichiometry of the metals prepared by co-precipitation could be written as M=Ni_{0.5}Co_{0.2}Mn_{0.3}.

Fig. 3 illustrates the final structural refinement patterns of the synthesized powder using X-ray diffraction data recorded at room temperature. According to phase identification using the International Center for Diffraction Data (ICDD) database, the XRD pattern of the synthesized powder shows that the materials consist of two phases: corresponded broadly to the β -phase of cobalt hydroxide (Co(OH)₂; ICDD no. 89-9616, no. 30-0443) [16], while the other approximately matched to that of deuterated cobalt oxyhydroxide (CoOOH; ICSD no. 56288) [17]. Each set of diffraction lines were displaced slightly from the expected (recorded) positions and due to the assumed additional inclusion of Ni and Mn metals, the lattice constants of each phase differed slightly from those of the original cobalt phases.

Structure refinement using X-ray diffraction data was performed to probe the structure and composition of the M(OH)₂ and MO(OH) phases in more detail. Initial crystal structural models for M(OH)₂ and MO(OH) was taken as the known structures of cobalt compounds, Co(OH)₂ (trigonal space group of $P\bar{3}m1$) and CoO(OH) (hexagonal $P6_3/mmc$), respectively [16,17].

All diffraction peaks observed in the powder X-ray diffraction pattern were indexed and parameters refined via the Le Bail refinement method using both lattice parameters and the space groups mentioned above [18]. The Le Bail refinement result indicates that there are no other phases present in the diffraction pattern other than the two phases described above. The result also therefore suggests that the transition metal elements (M) occupy the same crystallographic sites in the host lattices of M(OH)₂ and MO(OH), respectively. The crystallographic data were considered suitable for further structure refinement by the Rietveld method.

The occupancies of Ni, Cr and Mn (Ni:0.5, Co:0.2 and Mn:0.3) at the same crystallographic site were at the values defined by the EDS data and constrained to be unity in the structural refinement since from their respective form factors it is difficult to distinguish them based on X-ray diffraction data. After the preliminary

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