Synthesis and ionic conductivity of a high-entropy layered hydroxide

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A high-entropy layered hydroxide (HELH), in which Mg2+, Al3+, Co2+, Ni2+, Zn2+ were homogeneously distributed on two dimensions sheets, was synthesized for the first time. The HELH shows moderate thermal stability and hydroxide ion conductivity up to 10−3 S cm−1. This finding presents tremendous opportunities for emerging new two-dimensional high-entropy materials.

Key-words : Layered double hydroxide, LDH, 2D, High entropy alloy, Solid electrolyte

1. Introduction

High-entropy alloys are the alloys comprising five or more elements in near equimolar ratios.1,2) Their mechanical properties, including ultra high fracture toughness at cryogenic temperatures, excellent specific strength, are particularly attractive.2,3) Recently, this concept has been expanded to various oxides,5–6) nitrides7) and sulfides,8) oxysulfides,9) whose atomic sites are often occupied by multiple cations (typically five or more). Owing to their unique functionality, they have been applied as solid electrolytes,9) electrodes,10) superconductors,9,11,12) and capacitors.5,7) While most of the reported high-entropy materials have three-dimensional structures, examples of two-dimensional materials with high entropy are limited.9,10) Since two-dimensional structures have unique and anisotropic properties, such high-entropy materials are ideal candidates for emerging new properties.

Solid electrolytes with high ionic conductivity are in high demand for high-electrochemical devices. Among them, layered double hydroxides (LDHs) are known to show hydroxide ion conduction.13–16) LDHs are a family of anionic clays with a layered structure having the general formula of [M2+x−yM3−x+y(OH)2] [An−x/m zH2O].17) and variety of functionality has been developed.18–21) They consist of positively charged hydroxide sheets and interlayered cations. Hydroxide sheets contain divalent and trivalent cations and interlayer anions, such as Mg2+, Al3+, Ca2+, Cr3+, Mn2+, Mn5+, Fe2+3+, Co2+, Co3+, Ni2+, Ga3+, Cl−, Br−, CO32−, and NO3−. The Mg–Al LDH with CO3 anion is stable in alkaline solutions and exhibits high ionic conductivity of 10−2 S cm−1 at 80 °C in high humidity.13) The ratio and kinds of metals/ anions and particle size of the LDHs are known to affect their ionic conductivity.22–27) Furthermore, their nanosheets28) and nanocomposites29) show exceptionally high in-plane conductivities approaching ~10−1 S cm−1. However, their conductivity generally decreases under low-humidity conditions.13)

The diffusion of components in high entropy alloys is complicated, and depends on the temperature and nature of the diffusing components.30) Nonetheless, high ion conductivity in high-entropy oxide solid electrolytes30) motivates us to explore new layered hydroxides as electrolytes by the high-entropy strategy. In this study, we synthesized, for the first time, a high-entropy layered hydroxide (HELH), in which five cations were distributed homogeneously in the two dimensions (2D) sheets, and its thermal stability and ionic conductivity were investigated.

2. Experimental procedures

The HELH with CO32− anion was synthesized by the co-precipitation method. Mg(NO3)2·6H2O, Al(NO3)3·9H2O, Ni(NO3)2·6H2O, Co(NO3)2·6H2O, Zn(NO3)2·6H2O were dissolved in distilled water. This aqueous solution was added to 0.2 M Na2CO3 solution with stirring at room temperature. The suspension was heated in a Teflon-lined autoclave at 150 °C for 12 h, and then cooled. The precipitates thus formed were filtrated, washed with distilled water, and dried at 80 °C. Mg–Al LDH (Mg:Al = 3:1) with CO32− anion was synthesized according to the literature method30) for comparison of conductivity.

X-ray diffraction (XRD) pattern was recorded using an X-ray diffractometer (Miniflex 600, Rigaku) under Cu-Kα radiation. The diffraction peaks were indexed using Rigaku PDFXL software and then the lattice parameters of hexagonal cell were calculated using the least squares method.
Structure model was drawn using VESTA software.\textsuperscript{31)} X-ray absorption spectrum was measured at the BL5S1 of the Aichi Synchrotron Center (Proposal No. 2018D5013). The morphology and elemental mapping were studied using scanning transmission electron microscopy (STEM; HD-2000, Hitachi). The composition of metals was determined by inductively coupled plasma (ICP, SHIMADZU ICPE-9000). The thermal stability was evaluated by thermogravimetric and differential thermal analysis (TG–DTA; Thermo Plus TG 8120, Rigaku). Electrical conductivities of the pellets obtained by cold pressing under a pressure of 100 MPa were measured. Gold was evaporated on both sides of the pellets as the electrodes. The conductivity of the pellets was determined from impedance data obtained using an impedance analyzer (Solartron 1260; Solartron Analytical) at frequencies from 0.1 Hz to 10 MHz. Temperature and humidity were controlled by using thermohygrostat (IW221; Yamato Scientific).

3. Results and discussion

Figure 1 shows the XRD pattern of the synthesized HELH and its structural model. The main peaks were indexed as a hexagonal cell with the lattice parameters of $a = 0.30553(6)$ nm and $c = 2.2966(11)$ nm. The $c$-axis was shorter than that of Mg–Al LDH, as determined by the 003 diffraction peak ($c = 2.34$ nm).\textsuperscript{24)} Considering the larger ionic radii of transition metals (Co, Ni and Zn) has those of Mg and Al, smaller amount of water may account for this shorter $c$-axis. Small and sharp impurity peaks were indexed as wurtzite ZnO, and the origin of two other broad peaks at 28.86 and 33.28° was not clear. It is likely that ZnO and other impurities are thermodynamically comparable to HELH, and further optimization of synthesis condition may achieve selective synthesis of HEDH.\textsuperscript{32)}

The molar ratio of Mg:Al:Co:Ni:Zn determined by ICP was 1:1.00:0.996:0.993:1.00, which was close to the composition of the precursor solution used for its synthesis. It is quite natural to consider Mg, Ni, Zn cations are divalent and Al cation is trivalent in hydroxides. In order to examine the valence of Co, the X-ray absorption spectrum of Co–K edge was measured. The absorption edge of the HELH was close to divalent Co(NO$_3$)$_2$, indicating nearly divalent Co. (Fig. 2). Divalent Co accompanies less interlayered CO$_3^{2-}$ when compared with trivalent Co to keep charge neutrality.

The STEM image showed hexagonal platelet crystals having a size of 300 nm (Fig. 3). Energy dispersive X-ray spectrometry (EDX) mapping of each element showed a homogeneous distribution of these platelet crystals.

Figure 4 shows the TG curves of HELH and some LDHs. The first and second weight losses finished at 212 and 385 °C, respectively. These weight losses corresponded to the elimination of absorbed/interlayered water and the decomposition of HELH into oxides with the evolution of gases, respectively. It is worth noting that a qualitative understanding of different LDHs is difficult since each LDH has different species of cations, anions and water. Nonetheless, a small mass loss after heating suggested a relatively small amount of water and interlayered CO$_3^{2-}$ compared to the other LDHs.\textsuperscript{33,34)} This is also supported by divalent Co ion.

There was no significant improvement of its thermal stability as a result of increasing the entropy of its cation site in HELH. Since it is the common strategy to produce complex or high-entropy oxide by heating hydroxides,\textsuperscript{35,36)} the product after heating of HELH is likely to be complex oxide(s) stabilized by high-entropy effect. Assuming the reaction of this HELH into a high-entropy oxide upon heat treatment in air, the entropy gain of reactant, HELH, can be canceled by that of product, high-entropy oxide. Thus, it would be difficult to design HELH with high thermal stability via high entropy effect.

Figure 5 shows the temperature dependence of conductivity. The AC impedance were measured under relative humidity of 50 and 80%. The increase in temperature and relative humidity enhanced the total electrical conductivity (as measured by AC impedance) up to $10^{-3}$ S·cm$^{-1}$. The electrical conductivity measured by the DC polarization technique was $2 \times 10^{-5}$ S·cm$^{-1}$ at 80 °C under 80% relative humidity. This electrical conductivity was approx-
approximately two orders of magnitude lower than the total electronic conductivity. Thus, it was concluded that ionic conduction was dominant in this HELH. The ionic conductivity of HELH was lower than that of Mg–Al LDH under 50 and 80% relative humidity. Nonetheless, the humidity dependence of conductivities on HELH was small.

Although HELH would have various local structure on 2D sheets because of high-entropy cation site with five kinds of metals, this HELH does not show the significant advantage of its ion conductivity. Even though the origin of conductivity is still under debate, the conductivity can be dominantly affected by lower contents of CO$_3^{2-}$, but not by its local structure. We cannot deny the possible effect of impurity phase(s) on the ion conductivity. Variety of local structure in 2D HELH may have the opportunity for other applications, such as capacitors and catalysts.

4. Summary

In summary, a HELH with a homogeneous distribution of five cations was synthesized. This HELH was found to have moderate thermal stability and smaller dependence of ionic conductivity on humidity as compared to Mg–Al LDH. We believe that the flexible compositions and various local structure of HELHs can expand the variety of layered hydroxides, which can bring about new phenomena and application in two-dimensional materials.

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