Synthesis of High Entropy Layered Double Hydroxides for Capturing Iodide

Sujeong Lee [a], Ho Jin Ryu[a,b,]*
[a]Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology
[b]Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology
[*]Corresponding author: hojinryu@kaist.ac.kr

1. Introduction

Among 2D materials, layered double hydroxide (LDH) has widely been used in various applications such as battery, catalysis, and water treatment [1]. Specifically, its structure consists of positively charged laminates which make space for intercalated anions and water[2]. Thus, it could especially apply to capture the anionic radionuclides (I^- and IO_3^-) in the nuclear industry also[3].

However, the limited adsorption capacity and selectivity toward anionic species (I^- and IO_3^-) was the main issue in applying LDH to the nuclear industry. Thus, for solving this problem, some researchers used the method of calcination which removed the original anions in the LDH called calcined layered double hydroxide (CLDH) or layered double oxide (LDO) [4]. This process could make the structure more positively charged. Thus, the tendency of capturing anion species was stronger.

High entropy ceramics are recently investigated by researchers because the introduction of high entropy into the system has brought about advantages over conventional materials such as simple crystal structure, diversity of composition, irradiation resistance, and thermal stability. However, to the best of our knowledge, there are no published results available in the field of high entropy layered double hydroxide (HELH) for capturing anionic species.

In this study, we synthesized HELH as an adsorbent that might capture iodide (I^-) and iodate (IO_3^-). The newly synthesized system was characterized by XRD, SEM, TG-MS, ICP-MS, and XPS.

2. Methods and Experiment

2.1 Materials

Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, 99%, 237175), aluminum nitrate ($Al(NO_3)_2 \cdot 9H_2O$, 98%, 237973), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 98%, 239267), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99.999%, 203874), zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%, 228737), sodium hydroxide (NaOH, solution, 415413), sodium carbonate (Na_2CO_3, 99.999%, 451614) used in this study were a reagent grade and supplied by Sigma Aldrich.

2.2 Synthesis of high-entropy layered double hydroxide

Each metal nitrate constituent was dissolved in DI-water : ethanol = 1:1. Then, they were poured into one large jar together and made at a temperature of 70 °C. The pH of the solution was titrated till 10 through dropwise of 1M of NaOH and 0.5M of Na_2CO_3. Then 10 h aged slurry was washed several times till ion conductivity of washing water below 50 uS/cm and was dried at 70 °C for 10 h under a vacuum oven. The crushed powder (<150 μm) was used for the characterization.

2.3 Characterization

The crystal structure of synthesized Mg_3Al LDH, $(Mg_3CoNiZn)Al$ LDH and both LDO were investigated by X-ray diffractometry (XRD) (SmartLab, RIGAKU) with CuKα radiation at 45 kV and 200 mA. Data were collected in the range of 2θ=5-80° with a 0.01°/step and a scanning time of 10 s/step.

The microstructure of synthesized powders and cold sintered matrix was characterized by a Scanning Electron Microscopy (SEM) using a SU8230 (Hitachi) with 5 kV electron beam.

The thermal stability of the matrix was investigated by the thermogravimetric-mass spectrometry (TG-MS, STA449 F5 Jupiter, NETZCH, Agilent 5977B GC/MSD) from 70 °C to 1,000 °C with 10K/min and structured bound water and carbonate were analyzed too.

For verifying the successful synthesizing of HELH, ICP-MS (iCAP RQ, Thermofisher Scientific) detected the concentration of each constituent on the synthesized matrix. Furthermore, the oxidation status of each constituent was discovered by XPS (Nexsa G2, Thermo Scientific)

3. Results and Discussion

3.1. Synthesized LDH and HELH

The XRD patterns of Mg_3Al and HELH presented the hydrotalcite in both cases as shown in **Fig. 1**. The location of peaks at 11.4, 22.9, 34.4, and 60.3 was the same but there was a peak broadening in the HELH. This situation came from the compression or expansion of substitution of metal constituents into the main matrix[2].
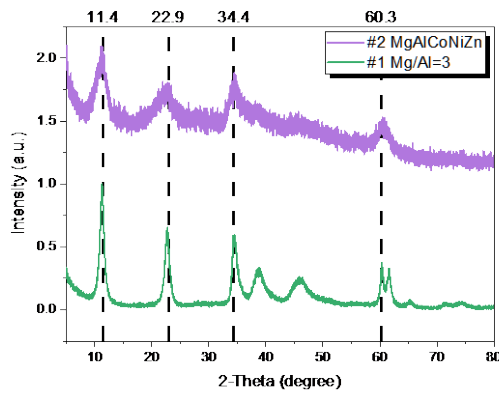
Fig. 1. XRD results of synthesized powders.

The morphology of layered double hydroxide was detected as a flower-like sheet. Also, the HELH system showed a similar morphology but a bit wrinkled flower-like sheet (**Fig. 2**)

TG-MS results showed us that both LDH and HELH contained water and carbonate. In the case of LDH, the mass reduction was two steps but HELH was three steps, meaning there was a new type of bounding species or bounding type in the system as shown in **Fig. 3**. The sum of water and carbonates was diminished from 42.8 % to 34.2 % from LDH to HELH based on the TG signals (black line).

The concentration of each metal element was quantitively detected through ICP-MS as shown in **Fig. 4**. The value showed the intended molar ratio of each element. It supported that a rapid co-precipitation at 70 ℃, pH 10 for 10 h could provide an environment where high entropy ceramic was fabricated.
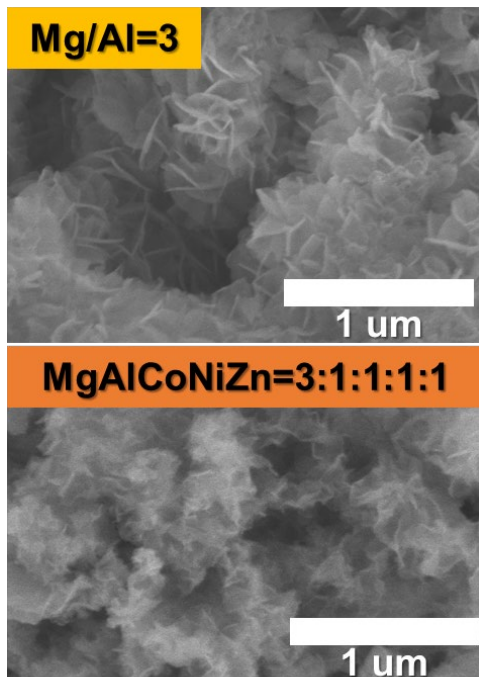

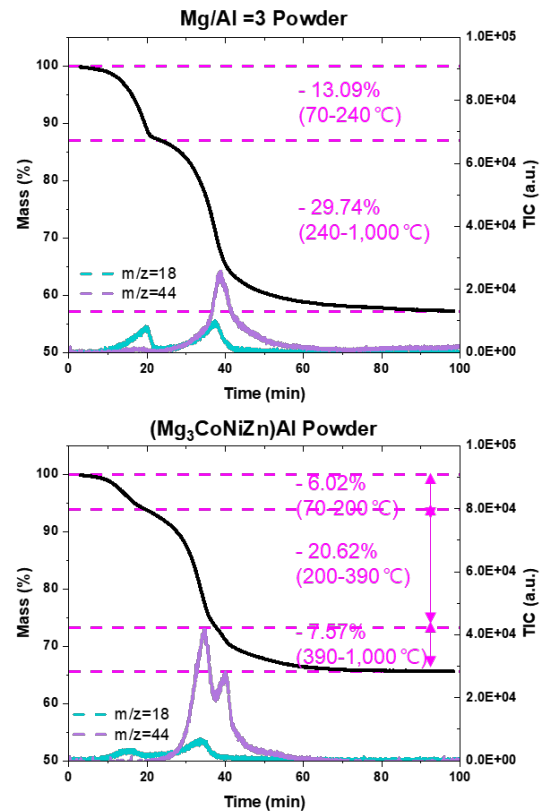
Fig. 2. SEM results of synthesized powders

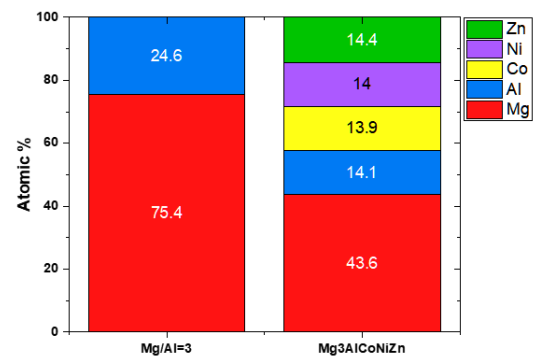**Fig. 3.** TG-MS results of synthesized powders

Fig. 4. ICP-MS results of synthesized powders

4. Conclusions

This study successfully synthesized high-entropy layered double hydroxide (HELH) by co-precipitation.The crystal structure of HELH was sustained as hydrotalcite but there was a peak broadening in HELH because of lattice distortion from additionally added constituents. The morphology of both synthesized powders was a flower-like sheet but HELH showed corrugation. It might also be an effect of lattice distortion. Based on the thermal stability result, amounts of moisture and carbonate in HELH were 8% reduced (42.8% to 34.2%) compared to binary LDH and

there was additional bonding between HELH and carbonate, indicating three steps of mass reduction.

REFERENCES

[1]   M. Kim, I. Oh, H. Choi, W. Jang, J. Song, C.S. Kim, J.W. Yoo, S. Cho, A solution-based route to compositionally complex metal oxide structures using high-entropy layered double hydroxides, Cell Reports Phys. Sci. 3 (2022) 100702. https://doi.org/10.1016/J.XCRP.2021.100702.

[2]   X. Yu, B. Wang, C. Wang, C. Zhuang, Y. Yao, Z. Li, C. Wu, J. Feng, Z. Zou, X. Yu, B. Wang, C. Wang, Y. Yao, Z. Li, C. Wu, J. Feng, Z. Zou, C. Zhuang, 2D High-Entropy Hydrotalcites, Small. 17 (2021) 2103412. https://doi.org/10.1002/SMLL.202103412.

[3]   F.L. Theiss, G.A. Ayoko, R.L. Frost, Iodide removal using LDH technology, Chem. Eng. J. 296 (2016) 300–309. https://doi.org/10.1016/J.CEJ.2016.02.039.

[4]   J. Kang, T.G. Levitskaia, S. Park, J. Kim, T. Varga, W. Um, Nanostructured MgFe and CoCr layered double hydroxides for removal and sequestration of iodine anions, Chem. Eng. J. 380 (2020) 122408. https://doi.org/10.1016/J.CEJ.2019.122408.

[5]   D. Sokol, A.N. Salak, M.G.S. Ferreira, A. Beganskiene, A. Kareiva, Bi-substituted Mg3Al–CO3 layered double hydroxides, J. Sol-Gel Sci. Technol. 85 (2018) 221–230. https://doi.org/10.1007/S10971-017-4506-9/FIGURES/15.

[6]   Q. Zhao, G. Chen, Z. Wang, M. Jiang, J. Lin, L. Zhang, L. Zhu, T. Duan, Efficient removal and immobilization of radioactive iodide and iodate from aqueous solutions by bismuth-based composite beads, Chem. Eng. J. 426 (2021) 131629. https://doi.org/10.1016/J.CEJ.2021.131629.

[7]   S.H. Lee, Y. Takahashi, Selective immobilization of iodide onto a novel bismuth-impregnated layered mixed metal oxide: Batch and EXAFS studies, J. Hazard. Mater. 384 (2020) 121223. https://doi.org/10.1016/J.JHAZMAT.2019.121223.