Binary and Ternary Layered Double Hydroxides for Iodine Decontamination

Sujeong Lee [a], Tien-Shee Chee[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

***Keywords :** Layered Double Hydroxides, Multi-elements, Iodine, Decontamination*

1. Introduction

Layered double hydroxide (LDH) as a representative 2D material has widely been used in various applications such as battery, catalysis, and water treatment [1]. There were three types of anions adsorption mechanisms of the LDH structure: surface adsorption, anion exchange, and ligand exchange [2]. Thus, the material could be applied to remove the anionic radionuclides (I^- and IO_3^-) from aqueous wastewater.

However, one of the limitations of the LDH structure is a lower selectivity towards iodine species during the existence of competing anions such as CO_3^{2-} and OH^-. Thus, there were several studies for overcoming the lower selectivity issues of LDH. One of the promising ways is tuning the metal elements of the LDH structure by using the combinations of Mg-Fe, Co-Al, Ni-Al, Co-Cr, and Ni-Cr [3–5]. Nonetheless, there was no logical reason for choosing a certain metal combination for the reversal selectivity. Thus, the mechanism of capturing anions onto LDHs remains a topic of ongoing debate.

Researchers have recently been exploring multielement ceramics due to their synergies such as tuning the electronic properties, defect features, and surface adsorption energetics. These provide unique and advantageous properties for adsorption [6]. However, to the best of our knowledge, there are no published results available in the field of multielement LDH for capturing anionic species. Thus, exploring the vast number of potential multielement LDH candidates is necessary to understand the possible synergies in anionic adsorption.

In this study, we synthesized selected 120 binary and ternary LDH as an adsorbent that might capture iodide (I^-) and iodate (IO_3^-). The feasibility of the system was evaluated by XRD, TG-MS, XRF, and IC.

2. Methods and Experiment

2.1 Materials

Metal nitrate salts, sodium hydroxide (NaOH, solution, 415413), and 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 binary and ternary layered double hydroxides

There are several LDH synthesis methods (hydrothermal, coprecipitation) and synthesis conditions (pH, temperature, aging time). Among these conditions, the coprecipitation (< pH 10, 25 ℃, 4 h) method was feasibly selected considering the number of samples.

The pH of the metal solution was titrated below 10 through dropwise of 1M of NaOH and 0.5M of Na_2CO_3. Then 4 h aged slurry was washed several times till the ion conductivity of washing water was below 100 uS/cm and was dried at 70 ℃ for 24 h under a vacuum oven. The crushed powder (<150 μm) was used for the characterization and stored at a vacuum desiccator.

2.3 Characterization

The crystal structure of synthesized all binary and ternary LDH was investigated by X-ray diffraction (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 thermal stability of the matrix was investigated by thermogravimetric analysis (TGA; STA 449 F5 Jupiter, NETZSCH)-differential thermal analysis (DTA)–mass spectrometry (MS; 5977B GC/MSD, Agilent), from 70 °C to 700 °C at a heating rate of 10 °C·min^{-1} and structured bound water and carbonate were analyzed too. For verifying the successful synthesizing of all binary and ternary LDH, an X-ray fluorescence spectrometer (XRF; ZSX Primus II, Rigaku) detected the concentration of each constituent on the synthesized matrix. Furthermore, the adsorption capacity of each LDH system was evaluated by ion chromatography (ICS-6000, Thermo Scientific).

3. Results and Discussion

3.1. Synthesized binary and ternary LDHs

The XRD patterns of some binary and ternary LDH presented the hydrotalcite, and others showed the secondary phases (malachite, bismutite, rhodochrosite) as shown in **Fig. 1**. This was because of the phase stability compared to metal carbonate which indicates with the solubility products, K_{sp}. With the XRD results, the synthesizability of each metal combination could be evaluated. The location of hydrotalcite dominant peaks at 11.4, 22.9, 34.4, and 60.3 was shown in the synthesized combination but there was a peak

broadening in some cases (mostly Cr-based). This situation resulted from the compression or expansion of lattice parameters [7].

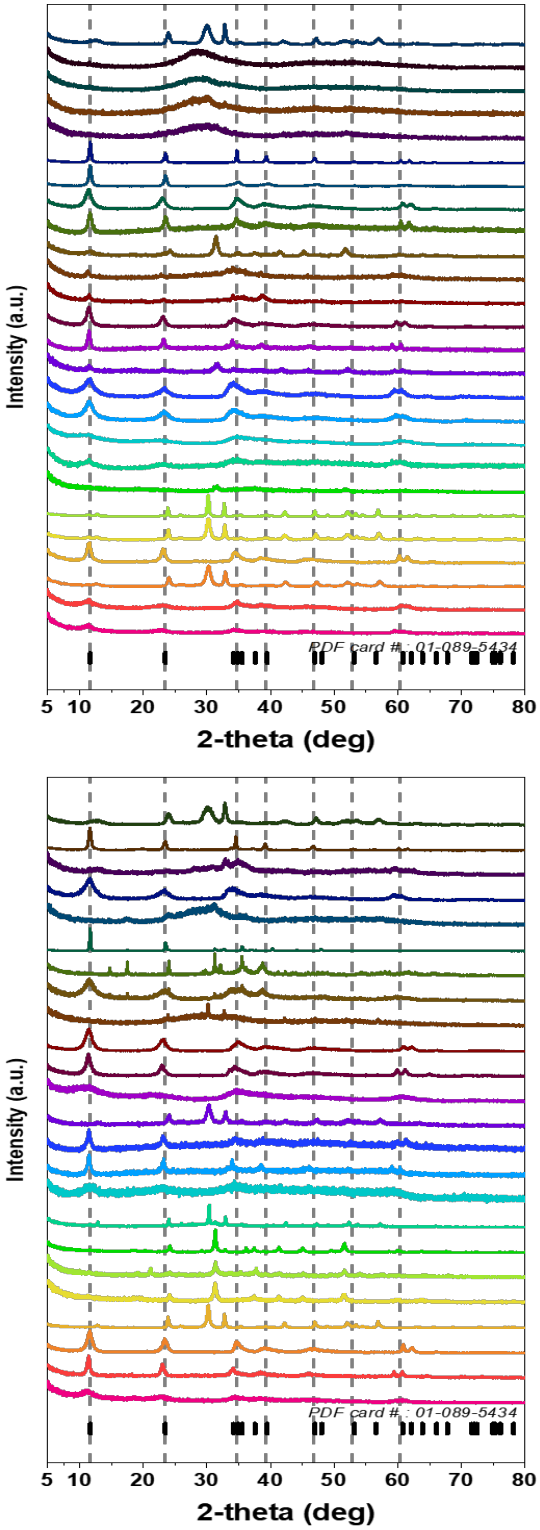

Fig. 1. XRD results of parts of binary and ternary LDHs

TG-MS results showed the presence of structural water (first mass reduction) and carbonate (second mass reduction) in the synthesized binary and ternary LDHs (**Fig. 2**). The different mass loss of each sample resulted from different amounts of structural water and carbonates during the synthesizing. Moreover, this might be related to the crystallinity of synthesized LDHs.

The concentration of each metal element was qualitatively detected through XRF as shown in **Fig. 3**. The value showed the intended relative molar ratio of each element. The yellow line indicated the designed ratio of divalent metal elements, but there were more loadings of trivalent metal elements. This effect would be affected by the adsorption capacity of iodine species, which is going to be updated.

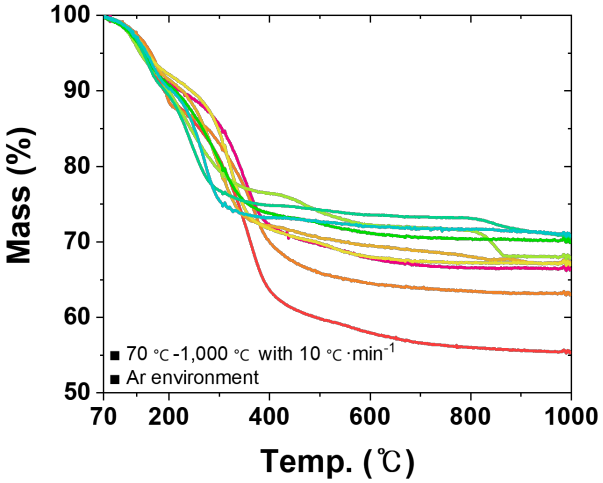

Fig. 2. TG-MS results of synthesized powders

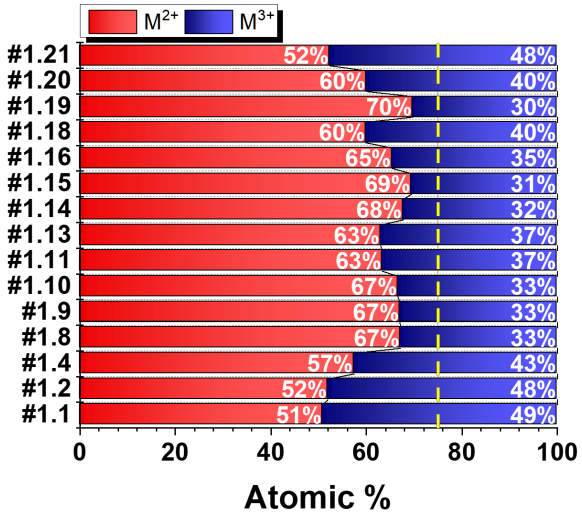

Fig. 3. XRF results of synthesized powders

4. Conclusions

This study was the first step in exploring the multielement layered double hydroxides. The synthesizability and the quality of selected binary and ternary LDHs were evaluated in the aspects of crystal structure, thermogravimetric, and concentration of each element. Then, these kinds of information

(synthesizability and adsorption performance) could be used for screening out multielement LDH in the future.

Acknowledgments

This study is supported by the KAI-NEET, KAIST, and NRF-2021M2D2A1A02043946.

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] J.-Y. Guo, X.-J. Zhao, W. Zhang, Y. Jie, X.-Y. Xu, H. Lu, H.-T. Song, H. Yan, Theoretical study on the mechanism of removing harmful anions from environment via Mg2Al layered double hydroxide, Appl. Surf. Sci. 637 (2023) 157759. https://doi.org/10.1016/J.APSUSC.2023.157759.

[3] 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.

[4] J. Kang, F. Cintron-Colon, H. Kim, J. Kim, T. Varga, Y. Du, O. Qafoku, W. Um, T.G. Levitskaia, Removal of iodine (I− and IO3−) from aqueous solutions using CoAl and NiAl layered double hydroxides, Chem. Eng. J. 430 (2022) 132788. https://doi.org/10.1016/J.CEJ.2021.132788.

[5] T.G. Levitskaia, S. Chatterjee, B.W. Arey, E.L. Campbell, Y. Hong, L. Kovarik, J.M. Peterson, N.K. Pence, J. Romero, V. Shutthanandan, B. Schwenzer, T. Varga, RedOx-controlled sorption of iodine anions by hydrotalcite composites, RSC Adv. 6 (2016) 76042–76055. https://doi.org/10.1039/C6RA13092E.

[6] Y. Zhang, T.C. Peck, G.K. Reddy, D. Banerjee, H. Jia, C.A. Roberts, C. Ling, Descriptor-Free Design of Multicomponent Catalysts, ACS Catal. 12 (2022) 10562–10571. https://doi.org/10.1021/acscatal.2c02807.

[7] 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.