

Preparation of Ion-Sieve Type (H)[M_{0.5}Mn_{1.5}]O₄ (M=Mg, Zn) and Their Lithium Adsorption Properties in Seawater

Kang-Sup Chung¹, Mi-Ae Kim¹, Hwan Lee¹, Yong-Jae Suh¹, Dae-Sup Kil¹,
B. C. Dave² and Jae-Chun Lee^{1,a}

¹Korea Institute of Geoscience and Mineral Resources(KIGAM), 30 Gajeong-dong, Yuseong-gu,
Daejeon 305-350, South Korea

²Department of Chemistry, Southern Illinois University, Carbondale, IL 62901, U.S.A.

^aCorresponding author: jclee@kigam.re.kr

Keywords: lithium adsorption, ion sieve, seawater

Abstract. Ion-sieve type manganese oxide spinels for the selective adsorption of lithium(Li) from seawater were prepared and their properties were examined. LiM_{0.5}Mn_{1.5}O₄ (M=Mg, Zn) precursors, in which part of manganese(Mn) was substituted with magnesium(Mg) or zinc(Zn), were synthesized through the solid-state reaction. The adsorbents, HM_{0.5}Mn_{1.5}O₄ (M=Mg, Zn) were derived from LiM_{0.5}Mn_{1.5}O₄ (M=Mg, Zn) by acid treatment. The optimum acid treatment was obtained at hydrochloric acid concentration of 0.5M and 0.3M for LiMg_{0.5}Mn_{1.5}O₄ and LiZn_{0.5}Mn_{1.5}O₄ precursors, respectively. Both cases required thrice-conducted acid treatments for the best results. The adsorption of Li by HMg_{0.5}Mn_{1.5}O₄ and HZn_{0.5}Mn_{1.5}O₄ adsorbents followed the Freundlich equation and the maximum adsorption of Li in artificial seawater was 30.3 mg/g and 33.1 mg/g, respectively. The adsorption efficiency of Li by HMg_{0.5}Mn_{1.5}O₄ and HZn_{0.5}Mn_{1.5}O₄ adsorbents in artificial seawater, in which Li concentration was adjusted to 0.2 mg/L, was as high as 88% and 89%.

Introduction

Developing a highly efficient adsorbent with high selectivity for lithium is important in the effective recovery of lithium dissolved in seawater. Spinel-structured ion-sieve type lithium manganese oxides have good selectivity for lithium ions in the aqueous phase of the topotactic extraction of lithium ions with acid. Because of their technological and commercial importance, these materials have been the focus of intensive studies as highly efficient adsorbents [1] or as electrolytes for lithium batteries [2]. Feng et al. [3], Liu et al.[4] and Chitrakar et al.[5] studied the Li⁺ extraction and insertion reactions of the lithium-selective adsorbent from seawater with LiM_{0.5}Mn_{1.5}O₄ (M = Mg, Zn, Al, Sb, etc.) in the aqueous phase. They reported that the Li⁺ ion adsorption of host materials increased by substituting monovalent, divalent, trivalent or pentavalent cations for some portions of the manganese ions in the spinel structure.

In this work, we prepared the LiM_{0.5}Mn_{1.5}O₄ (M = Mg, Zn) compounds through the solid-phase reaction. Ion sieve formation with thorough acid treatment was used to generate the ion-exchange adsorbent, which can selectively adsorb lithium ions dissolved in seawater. To form the groundwork for the creation of a high-performance lithium adsorbent, we examined the temperature of the thermal treatment, the characteristic of lithium ion elution during ion sieve formation, crystal structure, and the adsorption efficiency. We sought to recover lithium dissolved in seawater more efficiently than existing methods.

Experimental Procedure

Preparation of Li ion adsorbent. The precursor material of this work LiM_{0.5}Mn_{1.5}O₄ (M = Mg, Zn) compounds were synthesized using solid-state reaction. Li₂CO₃, [Mg(CH₃COO)₂•4H₂O or

$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] and MnCO_3 were mixed at a 1:0.5:1.5 molar ratio with mixer mill for 10 min, and the calcination process was done at 300–600°C for 4 hours. Finally, the calcined powder was furnace-cooled to room temperature for further observation. Through this process, $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (M = Mg, Zn) compounds were synthesized. The synthesized powder precursor was dissolved in HCl solution and stirred to elute lithium and to form a hole in the lithium site, producing an ion-sieve type adsorbent to selectively adsorb lithium ions in seawater. All chemicals have high purity levels, and were purchased from Aldrich (USA). Deionized water made by Milli-Q system (Millipore Company) was used.

Physical and chemical analysis. The lithium, magnesium, zinc and manganese contents of the $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (M=Mg, Zn) compounds were analyzed through atomic absorbance spectrometer (AAS, Perkin Elmer 5100ZL). The mean oxidation state (Z_{Mn}) of manganese was evaluated after determining the available oxygen through standard oxalic acid treatment [6]. The elution properties of lithium ions in the precursor compound during the acid treatment were examined with given varying HCl concentrations and frequencies at room temperature. To obtain the acid-treated sample, the prepared 1g of the precursor sample was immersed in a fixed concentration of HCl solution and stirred for 24 hrs per cycle. The concentrations of Li, Mg, Zn and Mn in the supernatant solution were determined through atomic absorption spectrometry, and the extractabilities of the metal ions were calculated accordingly. The change in the spinel structure of each sample before and after the acid treatment was examined using x-ray diffraction (XRD, Philips Xpert-MPD coupled with a Cu-K α radiation tube), and the surface area (m^2/g) and the pore size (cm^3/g) of the adsorbent compound were determined through the BET analyzer (Micromatrix, ASAT 2400).

Lithium ion adsorption from seawater. Adsorption properties of the prepared lithium ion adsorbent were tested through various experiments, that is, the effect of heat-treatment temperature during the synthesis of precursor, time required to reach equilibrium, amount of equilibrium adsorption by making the Freundlich isothermal line, and selectivity to lithium and regeneration after desorption.

Artificial seawater sample. For the exact quantitative analysis of the prepared adsorbent's adsorbing properties for lithium in seawater, artificial seawater made in the laboratory was used instead of natural seawater. The composition is almost similar to natural seawater - Na 1.07×10^4 mg/L, Mg 0.13×10^4 mg/L, K 0.04×10^4 mg/L, Ca 0.04×10^4 mg/L, Cl 1.68×10^4 mg/L, Li 0.2 mg/L and pH was adjusted to 8.01.

Results and Discussion

Preparation of Mg and Zn substituted manganese oxide adsorbents. To prepare the lithium adsorbent, spinel-structured $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (M=Mg, Zn) precursor compounds were synthesized through the solid-state reaction at 600°C for 4 hrs. Chemical analysis revealed that the chemical formula of synthesized samples were $(\text{Li})[\text{Mg}_{0.51}\text{Mn}_{1.49}]\text{O}_4$ and $(\text{Li}_{0.5}\text{Zn}_{0.54})[\text{Li}_{0.5}\text{Mn}_{1.48}]\text{O}_4$ and the mean oxidation states (Z_{Mn}) of manganese were 4.01 and 3.99, respectively.

Fig. 1 and 2 show the effect of the HCl concentration and the number of acid treatments on the extraction of metals from $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (M=Mg, Zn) precursors at 25°C. The optimum condition of acid treatment requires the highest extractability of lithium and the lowest extractability of manganese together. In the case of $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the reaction was observed thrice in 0.5-M HCl solution for 24 hours, and each reaction yielded the best result (Li extractability was over 95%; Mn was less than 5%); with $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the reaction was observed thrice in the 0.3 M-HCl solution for 24 hours, and each revealed the best result (Li extractability was over 99%; Mn was less than 2%).

Fig. 3 shows the XRD result of the process mentioned above, giving all diffractive results in the spinel structure. After the lithium elution by acid treatment, a well-maintained original structure was revealed.

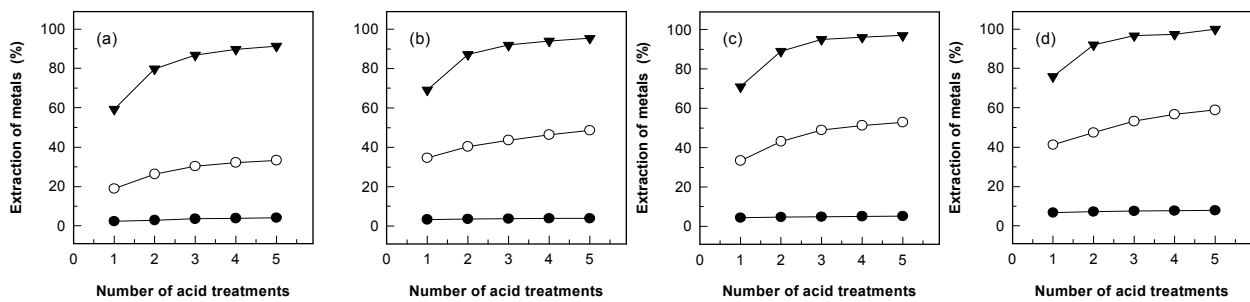


Fig. 1. Effect of HCl concentration and the number of acid treatments on the extraction of metals from $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ precursors at 25°C . (a) 0.1M HCl, (b) 0.3M HCl, (c) 0.5M HCl, (d) 1.0M HCl. (\blacktriangledown : Li, \circ : Mg, \bullet : Mn)

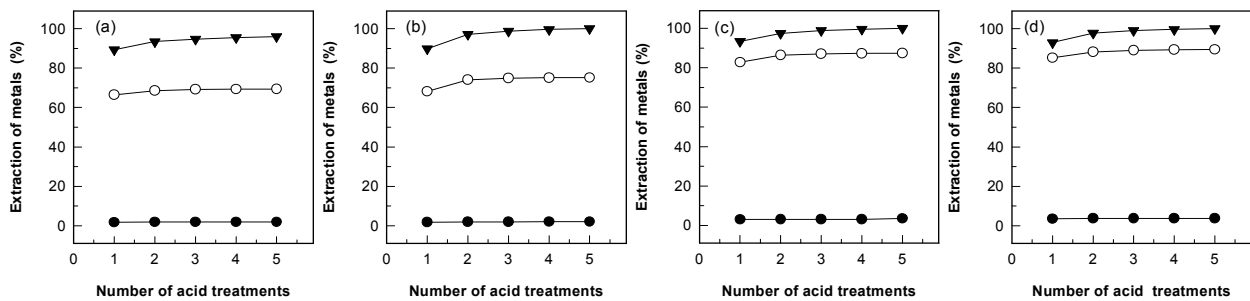


Fig. 2. Effect of HCl concentration and the number of acid treatments on the extraction of metals from $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$ precursors at 25°C . (a) 0.1M HCl, (b) 0.3M HCl, (c) 0.5M HCl, (d) 1.0M HCl. (\blacktriangledown : Li, \circ : Mg, \bullet : Mn)

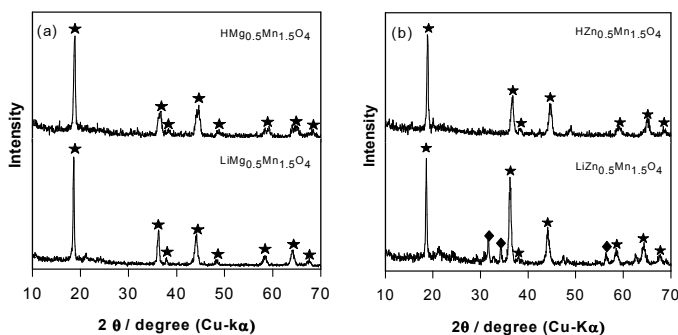


Fig. 3. XRD patterns of $\text{HMe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Me=Mg, Zn) adsorbents derived from $\text{LiMe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ precursors by acid treatment. (a) $\text{HMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$, (b) $\text{HZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$

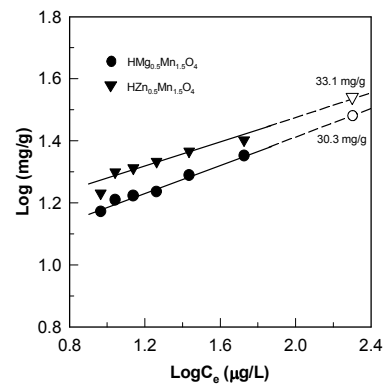


Fig. 4. Adsorption isotherms of lithium ion in artificial seawater. (Adsorbent dose: 10 ~ 60 mg, volume of seawater: 3L, reaction time: 4 days, temperature: 25°C)

Characteristics of lithium ion adsorption from seawater. Figure 4 shows the equilibrium adsorption amount of lithium per unit gram of adsorbent $x/m(\text{mg/g})$ for each equilibrium lithium ion concentration $C_e(\mu\text{g/L})$. The equilibrium adsorption amount was calculated using the Freundlich isothermal formula. The produced $\text{HMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{HZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$ adsorbent were changed from 10 mg to 60 mg and made to react in 3 L artificial seawater for 4 days. The equilibrium adsorption amount in artificial seawater was calculated as 30.3 mg/g and 33.1 mg/g. These values corresponded to the about four times enhanced value relative to the redox-type adsorbent HMn_2O_4 (7.8 mg/g).

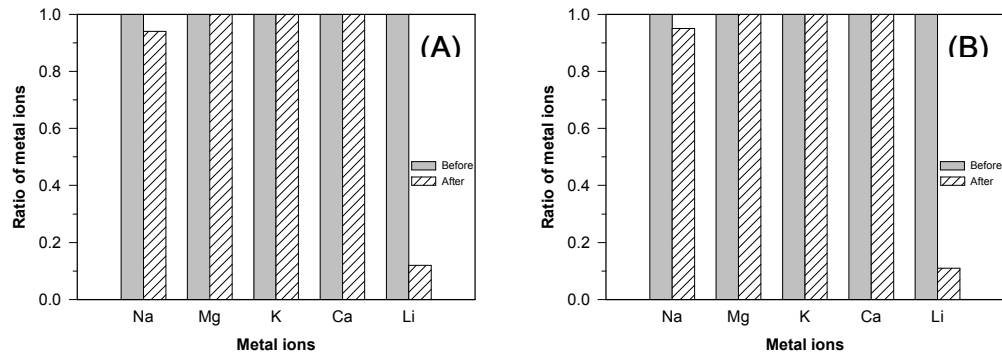


Fig. 5. Ratio of each metal ion concentration before and after adsorption reaction in artificial seawater with HZn_{0.5}Mn_{1.5}O₄ (A) and HMg_{0.5}Mn_{1.5}O₄ (B) adsorbent. (Adsorbent dose: 25 mg, volume of seawater: 3L, reaction time: 4 days, temperature: 25°C)

Selectivity of adsorbent. Figures 5 shows the changes in the concentration of metal ions that were included in artificial seawater after 25 mg of HMg_{0.5}Mn_{1.5}O₄ and HZn_{0.5}Mn_{1.5}O₄ adsorbent had been adsorbed in 3 L artificial seawater for 4 days. Although lithium showed 88% and 89% adsorption efficiency, Na showed only less than 6% and 5%. In the case of Mg, K, and Ca, the concentration rarely changed before and after the reaction, which showed the good selectivity of the produced HMg_{0.5}Mn_{1.5}O₄ and HZn_{0.5}Mn_{1.5}O₄ adsorbent in lithium ion.

Conclusions

Ion-sieve-type manganese oxide spinels, HM_{0.5}Mn_{1.5}O₄ (M=Mg, Zn) adsorbent were derived from LiM_{0.5}Mn_{1.5}O₄ (M=Mg, Zn) precursors through acid treatment and applied to react in artificial seawater to determine its properties. In the acid treatment, the reaction was thrice repeated in 0.5 M and 0.3 M HCl solution at 24 hours, and each cycle yielded the best results for LiMg_{0.5}Mn_{1.5}O₄ and LiZn_{0.5}Mn_{1.5}O₄ precursors, respectively. Produced HMg_{0.5}Mn_{1.5}O₄ and HZn_{0.5}Mn_{1.5}O₄ adsorbents adsorbed 30.3 mg and 33.1 mg lithium ion per adsorbent unit gram in artificial seawater. The adsorption efficiency of Li by HMg_{0.5}Mn_{1.5}O₄ and HZn_{0.5}Mn_{1.5}O₄ adsorbents in artificial seawater was as high as 88% and 89%. These results show that lithium ions can be separated and salvaged not only from seawater but also from waste materials containing lithium. Further studies on producing large amounts of adsorbent powder and the best means to dispense it can be carried out based on the results obtained in this study.

Acknowledgement

This research was supported by the Oceanic Mineral Resources Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Maritime Affairs Fisheries of Korea.

References

- [1] K. Chung, J. Lee, E. Kim, K. Lee, Y. Kim and K. Ooi: Mater Sci Forum. Vol. 449-452 (2004), p. 277
- [2] C.S. Johnson, N. Li, J.T. Vaughey, S.A. Hackney and M.M Thackeray: Electrochem Commun Vol. 7 (2005), p. 528
- [3] Q. Feng, H. Kanoh, Y. Miyai, and K. Ooi: Chem. Mater Vol. 7 (1995), p. 379
- [4] Y. Liu, Q. Feng, and K. Ooi: J. Colloid Interface Sci. Vol. 163 (1994), p. 130
- [5] R. Chitrakar, H. Kanoh, Y. Makita, Y. Miyai, and K. Ooi: Chem. Mater Vol. 10 (2000), p. 2325
- [6] JIS: *Methods for Determination of Active Oxygen in Manganese Ores*, M8233 (Japan 1969)