ADSORPTION CHARACTERISTICS OF LITHIUM ADSORBENT AIMED AT RECOVERY OF LITHIUM FROM GEOTHERMAL FLUID

Tomohiro Matsushita[1], Kotaro Yonezu[1], Yudzuru Inoue[1], Koichiro Watanabe[1] and Takushi Yokoyama[2]

[1]Department of Earth Resources Engineering, Faculty of Engineering, Kyushu University,

744 Motookaa Nishi-ku Fukuoka 819-0395 Japan

[2]Department of chemistry, Faculty of Science, Kyushu University, 6-10-1 Hakozaki Higashi-ku Fukuoka 812-8581 Japan

matsushita-tomohiro@mine.kyushu-u.ac.jp

Keywords: *lithium, geothermal fluid, spinel-type manganese, adsorbent, XPS and XAFS.*

ABSTRACT

In this study, the precursor (spinel-type lithium manganese oxide) was synthesised using the solid-state method following Kitajou (2005), and adsorbent (spinel-type manganese oxide) was prepared by extracting Li^+ from HCl solution. To investigate the effect of synthesis conditions on lithium adsorption properties, various conditions, including Li/Mn mole ratio (0.5, 0.75) and heating temperature (350℃, 450℃, 550℃) were selected. As a matter of practical convenience, simulated geothermal fluids were prepared at 100 mgl^{-1}(Li), 700 mgl^{-1}(SiO_2) and 1400 mgl^{-1}(Na), and the pH of the adsorption experiment was controlled at pH11 in order to prevent silica scaling during pretreatment. XPS and XAFS analyses were used to investigate the adsorption of lithium by the prepared adsorbent. The largest lithium uptake was found at a Li/Mn mole ratio of 0.75 and a heating temperature of 550℃. XPS analysis was used to measure the surface amount of lithium. Mn K-edge XAFS analysis revealed the redox type site in the adsorbent

1. INTRODUCTION

Lithium batteries are low weight and high energy density; and recently the price has been decreasing because large scale production is now possible (Snyder et al., 2009). It is expected that the demand for lithium batteries for electric vehicles will continue to increase in the future. Therefore, in the future the balance between lithium supply and lithium demand is likely to change, as some researchers have reported (Gruber et al., 2011; Kesler et al., 2012). On the other hand, usage of lithium will expand in other areas, for example, as a source of nuclear fusion, where lithium is used as a precursor for tritium, which may supply one of the future energy sources (Hoshino et al., 2011). Future supply uncertainties will remain because there are risks resulting from the uneven distribution of lithium resources in the world and the oligopoly of supply companies even if there are sufficient total lithium resources for future demand (Kawamoto and Tamashiro, 2010). From this point of view, it is important that the techniques related to lithium recovery from brine needs to be improved, and furthermore, it is also important that recovery of lithium from seawater or other lithium containing water will be established based on a long term perspective (Kawamoto and Tamasiro, 2010).

For the last few decades, many studies have been reported on lithium recovery from lithium containing water by various methods (Baba et al., 1984; Hano et al., 1992; Hayashi et al., 1987; Ikeshoji and Yoneya, 1984; Iwasaki et al., 1988; Kamata et al., 2002; Kitamura and Wada, 1978; Koyanaka, 1983; Koyanaka and Tsujimura, 1979; Miyai et al., 1986; Miyai et al., 2001; Onodera and Iwasaki, 1988; Onodera and Iwasaki, 1988; Ooi et al., 1983; Pauwels et al., 1995; Wada et al., 1983; Yanakase et al., 1983; Yoshinaga et al., 1986; Yoshinaga et al., 1982).

However, spinel-type manganese adsorbents have a relatively large amount of lithium uptake and high selectivity for lithium, and thus the use of this kind of spinel-type manganese adsorbent has also been reported by many researchers in the last two decades (Chitrakar et al., 2001; Feng et al., 1992; Kitajou et al., 2003; Kitajou et al., 2005; Kitajou et al., 2006; Miyai et al., 1993; Miyai et al., 1994; Miyai et al., 2002; Ooi et al., 1989; Ooi et al., 1991; Umeno et al., 2002; Wang et al., 2006; Yoshizuka et al., 2002; Yoshizuka, 2007; Yoshizuka, 2012; Zhang et al., 1991; Özgür, 2010).

The purpose of this study is to recover lithium from geothermal fluid from geothermal power plants. The potential for lithium recovery was suggested because relatively high concentrations of lithium exists in geothermal fluid (Koyanaka, 1983). Some studies of the recovery of lithium from geothermal fluid by using spinel-type manganese adsorbents have previously been reported (Hayashi et al., 1988; Kunugita et al., 1990; Park et al., 2012; Park et al., 2012).

In the current study we showed the adsorption performance of prepared spinel-type manganese adsorbent using a simulated geothermal fluid and observed the fine structure with X-ray analysis. According to Ooi (1991), lithium insertion occurs at three sites, namely: redox sites, Li^+-specific ion-exchange sites and nonspecific ion exchange sites (Ooi et al., 1991). In our study we consider the three types of sites.

2. EXPERIMENTAL

2.1 Preparation of adsorbent

The adsorbent was synthesized by the solid state reaction method following Kitajou (2005) (Kitajou et al., 2005). $LiOH•H_2O$ and Mn_3O_4 were mixed in the agate mortar at ratios of Li/Mn (mole ratio) = 0.5, 0.75 respectively and heated twice in an electric furnace, with the first calcination lasting for 5 hours and the second calcination also for 5 hours. Between the two calcinations the samples were mixed again with agate mortar. The first calcination temperatures were 300℃, 400℃ and 500℃ for each mole ratio, and second calcination used temperatures of 350℃, 450℃ and 550℃. After heating the samples were allowed to cool to room temperature in the electric furnace. These prepared precursor samples were named: LM-0.5,350, LM-0.5,450, LM-0.5,550, LM-0.75,350, LM-0.75,450 and LM-0.75,550, respectively, based on the prepared Li/Mn mole ratio and the calcination temperature (for example: LM-0.5,550 means the ratio Li/Mn = 0.5 and the second calcination temperature = 550℃).

The lithium extraction process was preceded by treating 2 g of the precursor with 2 L of HCl (0.5 M) for 12 h. After the acid treatment, the samples were filtered and washed with ultra pure water. Finally, adsorbents were prepared after being totally dried at room temperature. They were named as M-0.5,350, M-0.5,450, M-0.5,550, M-0.75,350, M-0.75,450 and M-0.75,550, respectively.

2.2 Lithium adsorption experiment

For the tests 0.2 g of each prepared adsorbent was added to 200 ml of simulated geothermal fluid, composed of 100 mgl^{-1} (Li), 1400 mgl^{-1} (Na) and 700 mgl^{-1} (SiO_2), and agitated for 24 hours with magnetic stirrer. The simulated geothermal fluid was designed to avoid silica scaling during pretreatment, and the pH value of 11 allows co-precipitation of magnesium (Kawabata, 2011). The samples were filtered and washed, then residues were used for X-ray analysis and filtered solutions were used for determination of lithium concentration in order to calculate the amount of lithium uptake. This calculation used the following equation:

$$q = \frac{C_0 - C}{w} L$$

where q is lithium uptake amount, C_0 is initial concentration in the simulated geothermal fluid, C is the lithium concentration at a certain time, w is weight of adsorbent and L is the volume of simulated geothermal fluid. All adsorption experiments were carried out at room temperature (25℃). Atomic absorption spectrometry (AAS) determined the lithium concentration (Thermo Fisher, ICE3300). Samples after the adsorption experiment were named: LM*-0.5,350, LM*-0.5,450, LM*-0.5,550, LM*-0.75,350, LM*-0.75,450 and LM*-0.75,550, respectively.

2.3 Physical Analysis

To observe the structural variation of the prepared samples, X-ray diffraction (XRD) analysis was performed (Rigaku, UltimaⅣ). Thermogravimetry - differential thermal analysis (TG-DTA) curves were obtained with EXSTAR7000 (Seiko Instrument Inc.).

2.4 XPS and XAFS Analysis

X-ray photoelectron spectrometer (XPS) analysis was carried out by AXIS165 (Shimazu/Kratos, Japan). The operation was performed with a monochromatic Al Kα X-ray source at 1486.6 eV. To obtain high resolution spectra, the pass energy was set at 40 eV (7 mA, 15 kV). All samples were fine powder, and so they were fixed on a sample block with carbon tape. The pressure was maintained at 10^{-7} Pa during measurement. All spectra were obtained at 0.1 eV steps. For correcting the binding energy, a carbon signal at 284.8 eV was selected to modify the spectra. The software VISOIN-2 (Shimazu) was used for data analyses.

X-ray absorption fine structure (XAFS) analysis was performed at BL14B2 in SPring-8, Japan. XAFS spectra of Mn K-edge were obtained in a transmission mode from Si (111) double crystal monochromator. Some of prepared samples were mixed with BN, and they were pressed into pellet form. $MnCl_2$, Mn_3O_4, MnO_2 and $KMnO_4$ were selected for reference samples. X-ray absorption near edge structure (XANES) spectra were acquired with Athena software.

3. RESULTS AND DISCUSSION

Figure 1 and 2 show the XRD patterns of precursors and adsorbents. All prepared precursors and adsorbents were mainly composed of spinel-type structure except for M-0.5,350. In general, their crystallinity increased with increasing calcination temperature. For the Li/Mn = 0.5 series, the α-Mn_2O_3 peak were seen more obviously than for the Li/Mn = 0.75 series. The structure change between precursor and adsorbent were observed from the peak shift of the XRD patterns. The peak shift due to lithium desorption became higher (higher 2 θ value) with increasing

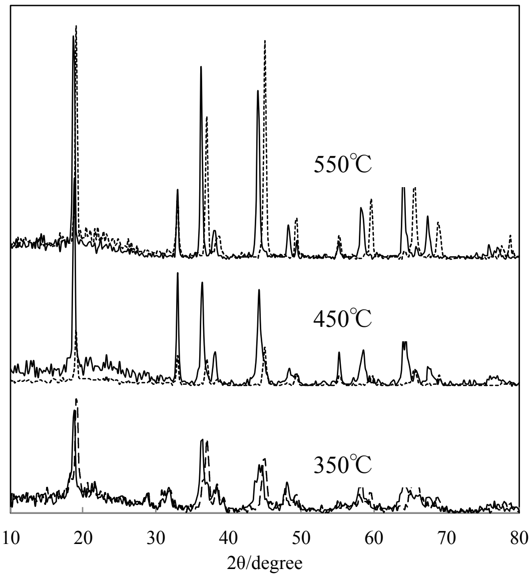

Figure 1: XRD patterns of precursors and adsorbents that were prepared for Li/Mn=0.5. Solid lines are precursors (LM-0.5,350, LM-0.5,450 and LM-0.5,550) and dotted lines are adsorbents (M-0.5,350, M-0.5,450 and M-0.5,550)

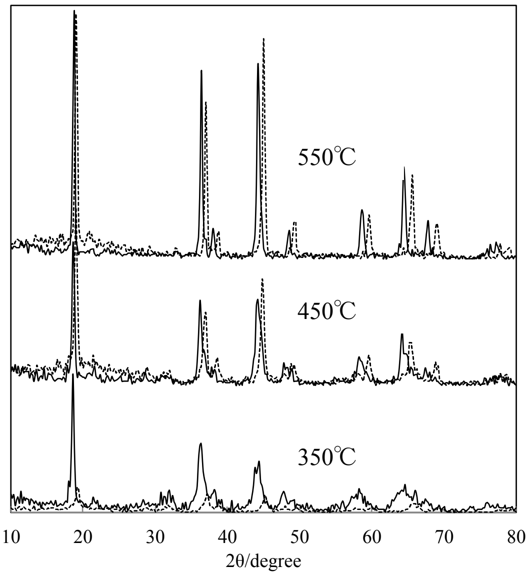

Figure 2: XRD patterns of precursors and adsorbents that were prepared for Li/Mn=0.75. Solid lines are precursors (LM-0.75,350, LM-0.75,450 and LM-0.75,550) and dotted lines are adsorbents (M-0.75,350, M-0.75, 450 and M-0.75,550).

diffraction angle. However, the peak of adsorbent was similar for each precursor. This means that lithium desorption was occurring topotatically. This kind of small peak shift between precursor and adsorbent has been reported for various synthesis conditions (Chitrakar et al., 2001; Feng et al., 1992; Kitajou et al., 2006; Ooi et al., 1991; Wang et al., 2006; Özgür, 2010). One reason for the peak shift derived from the difference in size between the lithium ion and hydrogen ion, because these peak shifts are related to the decrease of d value based on Bragg's law ($n\lambda=2d\sin\theta$) causing a change from the lithium ion (larger) to the hydrogen ion (smaller) (Özgür, 2010). Therefore, this change was expected from an ion exchange site. Another reason suggested was that the peak shift was derived from a redox type site due to the change of oxidation state from trivalent manganese to tetravalent manganese, which decreases the effective ionic radius (Feng et al., 1992). M-0.5,550 and M-0.75,550 kept the relative intensities of each of their precursors. Therefore, they strongly maintained their structure when lithium extraction occurred.

Figure 3 and 4 show the lithium uptake amount of each adsorbent for 24 hours. For the Li/Mn = 0.5 series, M-0.5,450 and M-0.5,550 adsorbed almost the same amount of lithium (15 mg/g). The maximum uptake amount for 24 hours was M-0.75,550, which adsorbed about 24 mgg^{-1} of lithium. In summary, under these conditions, the uptake t of lithium increased in the order: M-0.5,350, M-0.75,550 and M-0.75,550 (about 5 mgg^{-1}) <M-0.5,550 and M-0.5,550 (15 mgg^{-1}) < M-0.75,550 (24 mgg^{-1}). The lithium uptake occurred almost at the same speed for M-0.5,450, M-0.5,550 and M-0.75,550 in terms of the shape of the curve for the rate of lithium insertion. However, for M-0.75,550, the lithium uptake within 1 hour was remarkably large (14 mgg^{-1}) compared against M-0.5,450 and M-0.5,550 (approximately 7 mgg^{-1}). Therefore, this means that some fast-acting insertion sites were synthesized in M-0.75,550.

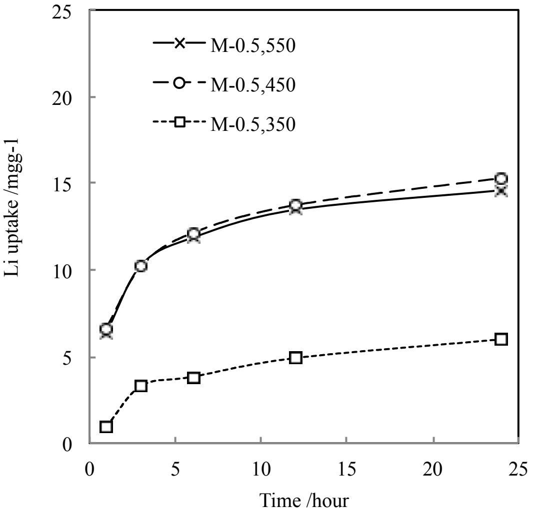

Figure 3: Lithium uptake amount for 24 hours from simulated geothermal fluid for adsorbents in the Li/Mn = 0.5 series. The amount of each adsorbent = 2 g and simulated geothermal fluid = 200 ml. pH = 11.

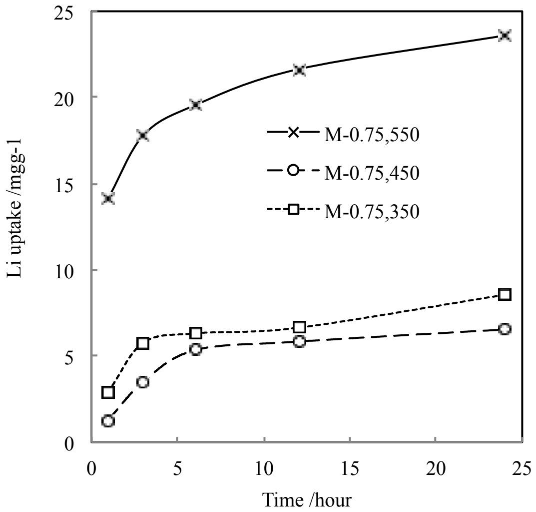

Figure 4: lithium uptake amount for 24 hours from simulated geothermal fluid for adsorbents in the Li/Mn =0.75 series. The amount of each adsorbent = 2 g and simulated geothermal fluid = 200 ml. pH = 11.

Figure 5 shows the TG-DTA curves for M-0.5,550 and M-0.75,550, representing the maximum uptake of each Li/Mn mole ratio. These weight losses were approximately 10% and 13% at 800℃ respectively. The first weight losses of M-0.75,550 occurred around 200℃ in combination with a broad endothermic peak. This endothermic peak corresponds to the condensation reaction of hydroxyl, which would synthesize an ion exchange site (Zhang et al., 1991). There are some irregular exothermic peaks from 180℃ to 270℃. According to Zhang (1991), the exothermic peak around 270℃ corresponds to a change from spinel-type manganese oxide to β-MnO$_2$, and this change is specific for the spinel-type manganese oxide. However, M-0.75,550 had two exothermic peak around 180℃ and 220℃, for reasons that are still unknown. The relatively sharp weight loss in combination with an endothermic peak at around 540℃ corresponds to phase change from MnO$_2$ to Mn$_2$O$_3$, and the weight loss is due to emission of oxygen gas. The weight loss between 100℃ to 300℃ shows good correlation with lithium uptake (Zhang et al., 1991), with 4% for M-0.5,550 and 7% for M-0.75,550. In light of the lithium uptake amount from the adsorption experiment, the difference of weight loss between M-0.5,550 and M-0.75,550 are matching. Meanwhile, the TGA curve for M-0.5,550 showed a broad exothermic peak around 270℃. However the peak was not shown clearly, and we could not make conclusions about this exothermic peak for M-0.5,500.

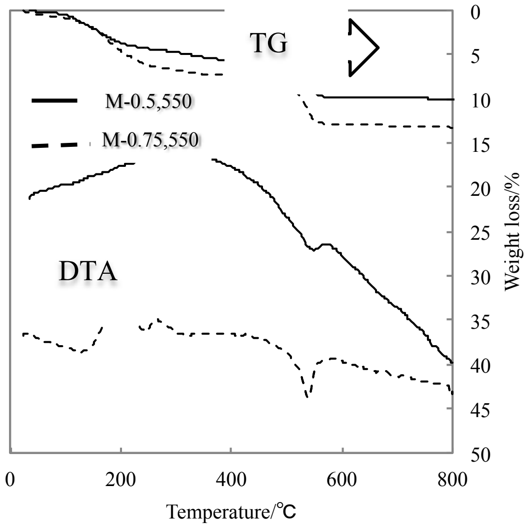

Figure 5: DTA-TG curves of M-0.5,550 and M-0.75,550 adsorbents.

To demonstrate the change in structure after lithium adsorption, XRD patterns of LM*-0.5,550 and LM*-0.75,550 are shown in Figure 6 and 7. The peak position got back to approximately same place as fo the precursors, and thus lithium adsorption occurred with while the spinel structure was maintained. Lithium insertion progressed topotaticaly as the lattice constant increased (Feng et al., 1992).

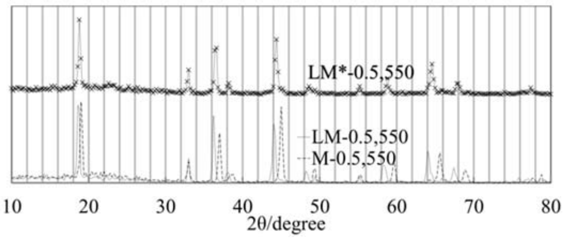

Figure 6: XRD patterns of precursor and adsorbent that were prepared at Li/Mn = 0.5, 550℃ (bottom) and sample of after lithium adsorption (top).

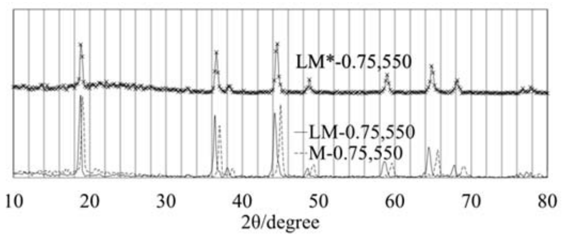

Figure 7: XRD patterns of precursor and adsorbent that were prepared at Li/Mn = 0.75, 550℃(bottom) and sample of after lithium adsorption (top).

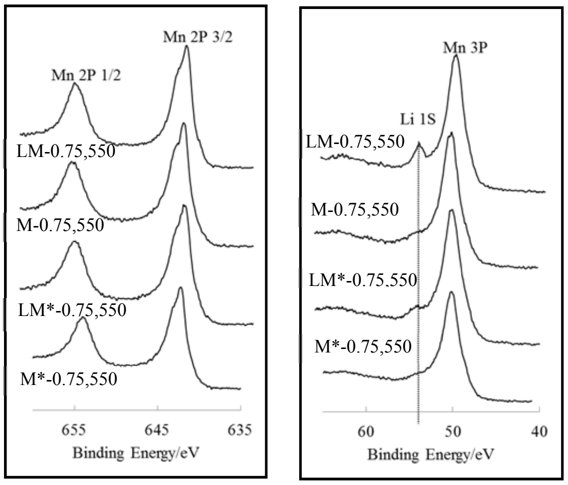

Figure 8: XPS spectra of LM-0.75,550, M-0.75,550, LM*-0.75,550 and M*-0.75,550 on Mn 2p, Mn 3p and Li 1s

Figure 8 shows the Mn 2p spectra, Mn 3p spectra and Li 1s spectra for LM-0.75,550, M-0.75,550, LM*-0.75,550 and M*-0.75,550 which were obtained after a second acid treatment. The Li 1s spectra relates to the existence of lithium on the surface of the sample. The result show the lithium on the surface of the precursor was almost removed with the acid treatment. While lithium is attached to the surface during the adsorption experiment, however the attached amount is less than for the precursor. With the second acid treatment, the surface lithium was dissolved again. The Li/Mn (mole ratio) on the surface of the samples was roughly calculated by the peak separation and their intensities. It showed approximately Li/Mn = 0.1.Lithium was attached on the surface after adsorption. However the amount of lithium on the surface was less than total amount of lithium that was calculated from dissolution of samples with H_2O_2 and HCl. It is suggested that lithium uptake mainly occurred inside the adsorbent.

Figure 9 showed Mn K-egde XANES spectra of LM-0.5,550, M-0.5,550 and LM*-0.5,550, and LM-0.75,550, M-0.75,550 and LM*-0.75,550. From the peak of XANES spectra around 6560 eV, the oxidation state of manganese was determined by comparing results with those from reference materials. For the Li/Mn = 0.5 series, the oxidation state of Mn was almost tetravalent for the precursor and the adsorbent. However, after lithium uptake, the oxidation state decreased, indicating that some tetravalent manganese changed to trivalent manganese. It was derived from redox type sites. For the Li/Mn = 0.75 series almost the same peak shift was observed when lithium adsorption occurred. As indicated by these shifts, both of the adsorbents have redox type sites in themselves.

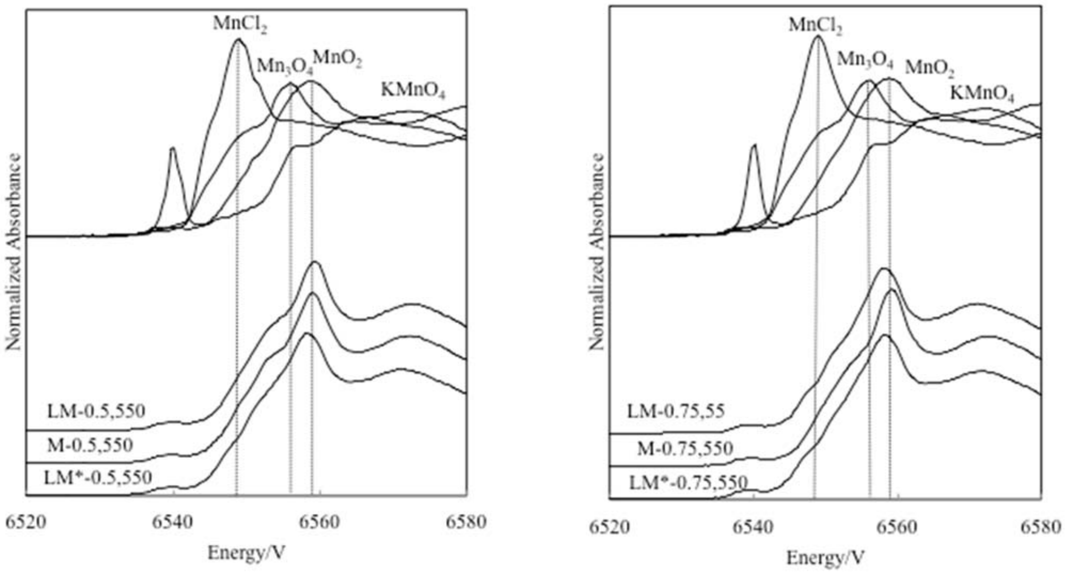

Figure 9: Mn K-edge XANES spectra of LM-0.5,550, M-0.5,550 and LM*-0.5,550 (left) and LM-0.75,550, M-0.75,550 and LM*-0.75,550 (right).

4. CONCLUSION

In this case, the largest lithium uptake was synthesized under the condition that the Li/Mn mole ratio was 0.75 and the heating temperature was 550℃. This adsorbent can adsorb about 24 mgg^{-1} of lithium in 24 hour. However in this study the lithium concentration of the simulated geothermal fluid was much higher than in a normal geothermal fluid and there were lower concentrations of other elements. Therefore, the actual lithium uptake amount would probably be less than the lithium uptake measured in this experiment. XPS analysis was used for rough classification of lithium absorption on the surface of the adsorbent. Lithium absorption occurred, but the amount was less than total lithium uptake amount, showing that lithium was adsorbed within the adsorbent. The prepared adsorbents had a redox type sites.

REFERENCES

Özgür, Cem. "Preparation and characterization of LiMn2O4 ion-sieve with high Li+ adsorption rate by ultrasonic spray pyrolysis." *Solid State Ionics* 181 (2010): 1425-1428.

Baba, Yoshinari, Katsutoshi Inoue, Akihiro Goto, and Issei Nakamori. "The Adsorption Mechanism of Lithium from Sea Water on 2.5MgO・Al2O3・xH2O (KW300)." *Bull. Soc. Sea WAter Sci. Jpn* 38, no. 3 (1984): 137-141.

Chitrakar, Ramesh, Hirofumi Kanoh, Yoshitaka Miyai, and Kenta Ooi. "Recovery of Lithium from Seawater Using Manganese Oxide Adsorbent (H1.6Mn1.6O4) Derived from Li1.6Mn1.6O4." *Ind. Eng. Chem. Res.* 40 (2001): 2054-2058.

Feng, Qi, Yoshitaka Miyai, Hirofumi Kanoh, and kenta Ooi. "Li+ Extraction/Insertion with Spinel-type Lithium Manganese Oxides. Characterization of Redox-Type and Ion-Exchange-Type Sites." *Langmuir* 8, no. 7 (1992): 1861-1867.

Gruber, Paul W., Pablo A. Medina, Gregory A. Keoleian, Stephen E. Kesler, Mark P. Everson, and Timothy J. Wallington. "Global Lithium Availability A Constraint for Electric Vehicles?" *Journal of Industrial Ecology* 15, no. 5 (2011): 760-775.

Hano, T, M Matsumoto, T Ohtake, N Egashira, and F Hori. "RECOVERY OF LITHIUM FROM GEOTHERMAL FLUID BY SOLVENT EXTRACTION TECHNIQUE." *SOLVENT EXTRACTION AND ION EXCHANGE* 10, no. 2 (1992): 195-206.

Hayashi, Hiromichi, Takashi Iwasaki, and Yoshio Onodera. "Preparation of λ-MnO2 and Lithium Adsorption from Geothermal Brine." *NIPPON KAGAKU KAISHI* 11 (1988): 1906-1908.

Hayashi, Hiromichi, Takashi Iwasaki, and Yoshio Onodera. "The Evaluation of Inorganic Materials as the Lithium Selective Adsorbents Applicable to Geothermal Brine." *Tohoku Kogyo Gijyutu Shikenjo Houkoku*, no. 21 (1987): 33-39.

Ikeshoji, Tamio, and Michio Yoneya. "A review for Source Recovery from Geothermal Hot Water." *Tohoku Kogyo Gijyutu Shikenjo Houkoku*, no. 17 (1984): 57-66.

Iwasaki, Takashi, Yoshio Onodera, Hiromichi Hayashi, and Kazuo Torii. "Adsorption of Lithium on Dioctahedal Smectites under Hydrothermal Conditions." *Journal of the Clay Science Society of Japan* 28, no. 3 (1988): 155-164.

Kamata, Ichiro, Kosuke Araki, Masahiro Goto, Akihiro Sakaguchi, Fumiyuki Nakashio, and shintaro Furusaki. "Li(Ⅰ) Seletive Resins Prepared by Means of Molecular Imprinting Technique Utilizing Synergistic Dffect." *Bull. Soc. Sea Water Sci. Jpn* 56, no. 3 (2002): 228-233.

Kawamoto, Hiroshi, and Wakana Tamashiro. "Lithium Shigen no Kyoukyu to Jidousyayoujuyou no Doukou." *Science & Technology Trends*, December 2010: 17-29.

Kesler, Stephen E., Paul W. Gruber, Pablo A. Medina, Gregory A. Keoleian, Mark P. Everson, and Timothy J. Wallington. "Global lithium resources: Relative importance of pegmatite, brine and other deposits." *Ore Geology Reviews* 48 (2012): 55-69.

Kitajou, Ayuko, Marek Holba, Takuya Suzuki, Syouhei Nishihama, and Kazuharu Yoshizuka. "Selective Recovery System of Lithium from Seawater Using a Novel Granulated λ-MnO2 Adsorbent." *J. Ion Exchange* 16, no. 1 (2005): 49-54.

Kitajou, Ayuko, Takuya Suzuki, Syouhei Nishihama, and Kazuharu Yoshizuka. "SELECTIVE RECOVERY OF LITHIUM FROM SEAWATER USING A NOVEL MnO2 TYPE ADSORBENT Ⅱ-ENHANCEMENT OF LITHIUM ION SELECTIVITY OF THE ADSORBENT." *Ars Separatoria Acta* 2 (2003): 97-106.

Kitajou, Ayuko, Yasuhiro Suzuka, Shouhei Nishihama, Takuya Suzuki, and Kazuharu Yoshizuka. "Development of λ-MnO2 Adsorbent toward the Practical Recovery of Lithium from Seawater." *J. Ion Exchange* 17, no. 1 (2006): 7-13.

Kitajou, Ayuko, Yasuhiro Suzuka, Syouhei Nishihama, Takuya Suzuki, and Kazuharu Yoshizuka. "Development of λ-MnO2 Adsorbent toward the Practical Recovery of Lithium from Seawater." *J. Ion Exchange* 17, no. 1 (2006): 7-13.

Kitamura, Takao, and Hideo Wada. "Properties of Adsorbents Composed of Hydrous Aluminium Oxide, and its Selective Adsorption of Lithium from Sea Water." (Bulletin of the Society of Sea Water Science) 32, no. 2 (1978): 78-81.

Koyanaka, Yoshio. "Natural Content of Lithium in Effluent of Geothermal Power Plant and the Development of Collection Technique." *Flotation* 30, no. 1 (1983): 11-17.

Koyanaka, Yoshio, and Tomotaka Tsujimura. "Concentration of Lithium in Sea Water by Ion Retadation Resin." *Flotation* 26, no. 4 (1979): 169-172.

Kunugita, Eiichi, Jonghwa Kim, and Isao Komasawa. "Process for Recovery and Purification of Lithium from Dilute Sources." *KAGAKU KOGAKU RONBUNSHU* 16, no. 5 (1990): 1045-1051.

Miyai, yoshitaka, Hirofumi Kanoh, Ramesh Chitrakar, and Kenta Ooi. "Lithium Adsorptive Properties of a New Type of Ion-sieve Adsorbent Based on Li2Cr(PO4)1.67." *Bull. Soc Sea Water Sci. Jpn* 55, no. 2 (2001): 97-102.

Miyai, Yoshitaka, Kenta Ooi, and Shunsaku Katoh. "Column Adsorption with Granular Manganese Oxide Adsorbent." *Bulletin of the Society of Sea Water Science, Japan* 47, no. 2 (1993): 81-85.

Miyai, Yoshitaka, Kenta Ooi, and Shunsaku Katoh. "Recovery of Lithium from Geothermal fluid. Ⅲ. Adsorption of Lithium by γ-Manganese(Ⅳ) Oxide." *Journal of the Mining and Metallurgical Institute of Japan* 102, no. 1179 (1986): 29-32.

Miyai, Yoshitaka, Kenta Ooi, and Shunsaku Katoh. "Study of Preparation Conditions of Ion-Sieve Type Manganese Oxides." *Bulletin of the Society of Sea Water Science, Japan* 56, no. 1 (2002): 57-63.

Miyai, Yoshitaka, Kenta Ooi, Tomonobu Nishimura, and Jyunji Kumamoto. "Lithium Adsorptive Properties of a New Selective Adsorbent Derivd from Li1.33Mn1.67O4." *Bull. Soc. Sea Water Sci., Jpn* 48, no. 6 (1994): 411-415.

Onodera, Yoshio, and Takashi Iwasaki. "Accumulation Mechanism of Lithium Ions by Dawsonite." *Journal of the Mining and Metallurgical Institute of Japan*, no. 104 (1988): 1201.

Onodera, Yoshio, and TAkashi Iwasaki. "Selective Collection of Lithium in Hot Ground Water by Dawsonite." *Journal of the Mining and Metallurgical Institute of Japan* 104, no. 1200 (1988): 21-25.

Ooi, Kenta, Takao Kitamura, Hideo Wada, and Shunsaku Katoh. "Recovery of Lithium from Geothermal fluid. Ⅱ. Lithium Ion Adsorption by Hydrous Tin (Ⅳ) Oxide." *Journal of the Mining and Metallurgical Institute of Japan* 99, no. 1148 (1983): 51-54.

Ooi, Kenta, Yoshitaka Miyai, and Jitsuo Sakakihara. "Mechanism of Li+ Insertion in Spinel-type Manganese Oxide. Redox and Ion-Exchange Reactions." *Langmuir* 7, no. 6 (1991): 1991.

Ooi, Kenta, Yoshitaka Miyai, Shunsaku Katoh, Hiroshi Maeda, and Mitsuo Abe. "Topotatic Li+ Insertion to λ-MnO2 in the Aqueous Phase." *Langmuir* 5, no. 1 (1989): 150-157.

Park, Jeongeon, Hideki Sato, Syouhei Nishihama, and Kazuharu Yoshizuka. "Separation and Recovery of Lithium from Geothermal fluid by Sequential Adsorption Process with λ-MnO2 and TiO2." *Ion Exchange letters* 5 (2012): 1-5.

Park, Jeongeon, Hideki Sato, Syouhei Nishiyama, and Kazuharu Yoshizuka. "LITHIUM RECOVERY FROM GEOTHERMAL FLUID BY COMBINED ADSORPTION METHODS." *Solvent Extraction and Ion Exchange* 30 (2012): 398-404.

Pauwels, Héléne, Michel Brach, and Christian Fouillac. "Study of Li+ adsorption onto polymeric aluminium(Ⅲ) hydroxide for application in the treatment of geothermal fluids." *Collids Surfaces A: Physicochem. Eng. Aspects*, no. 100 (1995): 73-82.

Umeno, Aya, Yoshitaka Miyai, Norio Takagi, Ramesh Chitrakar, Kohji Sakane, and Kenta Ooi. "Preparation and Adsorptive Properties of Membrane-Type Adsorbents for Lithium Recovery from Seawater." *Ind. Eng. Chem. Res.* 41, no. 17 (2002): 4281-4287.

Wada, Hideo, Takao Kitamura, Kenta Ooi, and Shunsaku Katoh. "Recovery of Lithium from Geothermal fluid by Amorphous Hydrous Aluminium Oxide." *Journal of the Mining and Metallurgical Institute of Japan* 99, no. 1145 (1983): 69-72.

Wang , Lu, Wei Ma, Ru Liu, Li Hai Yan, and Meng Chang Gong. "Correlation between Li+ adsorption capacity and the preparation conditions of spinel lithium manganese precursor." *Solid State Ionics* 177 (2006): 1421-1428.

Yanakase, Kenjiro, Tetsutaro Yoshinaga, Kentaro Kawano, and Toshikazu Matsuoka. "The Recovery of Lithium from Geothermal fluid in the Hachobaru Area of Kyushu, Japan." *Bull. Chem. Soc. Jpn* 56, no. 8 (1983): 2490-2498.

Yoshinaga, Tetsutaro, Kenjiro Yanagase, Kentaro Kawano, and Yasuaki Ueda. "RECOVERY OF LITHIUM FROM GEOTHERMAL FLUID IN THE HATCHOBARU AND OHTAKE AREA IN KYUSHU." *Proceeding of the New Zealand geothermal workshop*, no. 2 (1982): 329-332.

Yoshinaga, Tetsutaro, Kentaro Kawano, and Hirotsugu Imoto. "Basic Study on Lithium Recovery from Lithium Containing Solution." *Bull. Chem. Soc. Jpn* 59 (1986): 1207-1213.

Yoshizuka, Kazuharu. "Performance Evaluation of Benchmark Plant for Selective Lithium Recovery from Seawater." *J. Ion Exchange* 18, no. 4 (2007): 450-453.

Yoshizuka, Kazuharu. "Practical Recovery of Lithium from Seawater." *J. Ion Exchange* 23, no. 3 (2012): 59-65.

Yoshizuka, Kazuharu, Kenji Fukui, and Katsutoshi Inoue. "SELECTIVE RECOVERY OF LITHIUM FROM SEAWATER USING A NOVEL MnO2 TYPE ADSORBENT." *Ars Separatoria Acta* 1 (2002): 79-86.

Zhang, ShaoCheng, Tomonobu Nishimura, and Kenta Ooi. "Relation between PhysicochemicalProperties and Lithium Adsorptivity of Manganese Oxide Adsorbent." *Bulletin of the Society of Sea Water Science, Japan* 45, no. 6 (1991): 333-337.