

§17. Development of Lithium Recovery Technology for Resource Supply to Nuclear Fusion Reactor

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The deuterium-tritium (D-T) fusion reactor is expected to be a system to provide the main electricity in the future without any serious release of hazardous products such as a radioisotope of tritium, and it is the easiest fusion reaction to achieve. Lithium will be required in amounts dependent on the reactor design concept. When liquid lithium is used as a tritium breeder and a coolant, lithium inventories are large¹⁾. Lithium is now recovered from the mines and from salt lakes which contains about 14 millions tons of lithium. Although the amount of lithium in those resources is quite insufficient at this point, alternative resources should be found to satisfy lithium inventories for nuclear fusion plants and the increasing demand for battery and so on in the near future. Seawater, which contains 2300 hundred million tons of lithium in total, has thus recently become an attractive source of this element and the separation and recovery of lithium from seawater by co-precipitation, solvent extraction, adsorption, etc. have been investigated. Among these techniques, the adsorption method is suitable for recovery of lithium from seawater because certain inorganic ion-exchange materials show extremely high selectivity for lithium ion only. Among the inorganic adsorbents, spinel-type manganese oxides are interesting materials because of their extremely high affinity toward lithium ions only.

In this study, we prepared the lithium adsorbent by elution of spinel-type lithium di-manganese-tetra-oxide (LiMn_2O_4) using two preparation methods, and the kinetics of the adsorbent for lithium ions in seawater was examined.

Two mixtures were prepared as starting materials. One is the mixture of powdered Mn_3O_4 and powdered $\text{LiOH} \cdot \text{H}_2\text{O}$, and the other is the mixture of powdered Mn_3O_4 and LiOH aqueous solution. The each mixed molar ratio of Li/Mn is 0.5, and the each mixture ground for 15 min. The mixture was sintered at 425 °C for 5 h in an electric oven, and then cooled to room temperature. The sintered mixture was ground again for 15 min, and was again sintered at 500 °C for 5 h with the electric oven. After slow cooling in the electric oven for 12 h, Li-type adsorbent (LiMn_2O_4) was obtained as an intermediate product. The Li-type adsorbent was treated with 1.0 mol/L HCl solution (overnight, 5-times), for the exchange between Li^+ in the adsorbent and H^+ in HCl solution to obtain H-type adsorbent (HMn_2O_4). The ratio of H^+ in HCl solution to Li^+ in the adsorbent was more than 40. The Li-type and H-type adsorbents obtained from powder mixture represent as LiMn_2O_4 -1 and HMn_2O_4 -1, and those obtained from slurry as LiMn_2O_4 -2 and HMn_2O_4 -2.

The composition of the Li-type and H-type adsorbents were determined by an inductively coupled plasma emission spectrophotometer (ICP-AES, Seiko instruments, SPS3000), following the powder dissolving in the mixture of 30 wt.% H_2O_2 and 1 mol/L HCl. The characteristics of the crystal structure of H-type and Li-type adsorbents were recognized using a powder X-ray diffractometer (XRD, Rigaku, Rint-2500).

The H-type powder adsorbent (0.1 g) was added into modified seawater solution with 1 mmol/L Li ion (200 mL), which was prepared by adding LiCl into seawater obtained from Imari Bay, Saga prefecture, and stirred with magnetic stirrer at 5, 25 and 60 °C. During stirring, aliquots (2.5 mL) of each slurry were removed at varying time intervals to monitor the reaction process over a period of 24 h. The aliquots were filtered, and the concentrations of Li^+ in the filtrate were analyzed by ICP-AES. The corresponding adsorption amounts (q_{Li} [mmol/g]) and recovery ratio (R [%]) were determined from the material balance, as follows.

$$q_{\text{Li}} = (C_{\text{Li}0} - C_{\text{Li}}) \cdot L/w \quad (1)$$

$$R = (C_{\text{Li}0} - C_{\text{Li}})/C_{\text{Li}0} \times 100 \quad (2)$$

where $C_{\text{Li}0}$ and C_{Li} are initial and equilibrium concentrations of Li^+ in the aqueous phase [mmol/L], L is volume of aqueous solution [L], and w is weight of adsorbent [g]. pH of aqueous phase was measured with a pH meter (Horiba F-23).

Fig. 1 shows the XRD patterns of intermediates, LiMn_2O_4 , and the obtained adsorbents, HMn_2O_4 . Intermediates from both starting materials indicate the peaks of spinel structure, and the both adsorbents after HCl treatment indicate the same peak patterns. It is considered that H-type adsorbent can be prepared by keeping the crystal structure. It is noted that approximately 40 % of Li^+ was eluted from the both intermediate, LiMn_2O_4 , by 5 times acid treatment.

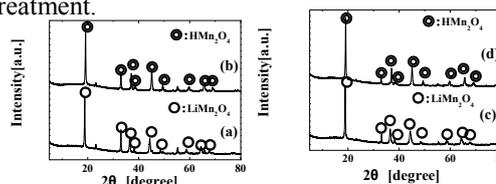


Fig. 1. XRD patterns of (a) LiMn_2O_4 -1, (b) HMn_2O_4 -1, (c) LiMn_2O_4 -2 and (d) HMn_2O_4 -2.

Fig. 2 shows the Li^+ recovery from modified seawater using (a) HMn_2O_4 -1 and (b) HMn_2O_4 -2. Lithium can be recovered from seawater using both adsorbents.

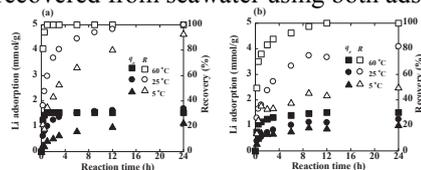


Fig. 2. Rate of lithium adsorption from modified seawater using the obtained adsorbents, (a) HMn_2O_4 -1 and (b) HMn_2O_4 -2. pH is kept at 7-9 during reaction.

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