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Improvement of lithium adsorption capacity of porous cylinder-type lithium manganese oxide through introduction of additive

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HIGHLIGHTS

- Fabrication of cylinder-type LMO for the practical adsorption process of lithium.
- Synthesis of lithium ion selective porous cylinder-type LMO adsorbents by adding Na_2CO_3 as an additive.
- Manipulation of the relative porosity of LMO adsorbents through the heat treatment and delithiation step with 0.3 M HCl.
- The porous LMO with Na_2CO_3 loading of 7 wt% exhibited the highest lithium uptake level of 19.19 mg g^{-1}.

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ABSTRACT

Spinel lithium manganese oxides (LMOs) have been widely used as an adsorbent for the recovery of lithium from aqueous solutions due to its high selectivity. Here, we manipulated the powders into a cylindrical shape using water glass as a binder together with the reactants (Li_2CO_3 and $MnCO_3$). The cylinder-type LMO showed a rather limited maximum adsorption capacity of 15.06 mg g^{-1} compared with that of 27.62 mg g^{-1} with LMO powder. To overcome this drawback, the effect of (Na_2CO_3) additive on the maximum adsorption capacity of cylinder-type LMO was evaluated by varying the additive amounts from 2 to 10 wt%. The maximum adsorption capacity increased to 19.19 mg g^{-1} by adding 7 wt% Na_2CO_3 as an additive. The enhanced adsorption capacity was believed to be the result of increased surface area due to the additional internal channels and pores introduced during the acid treatment. This study clearly demonstrates that the adsorption properties of cylinder-type LMO can be improved by using additives while maintaining the structural stability even after the heat treatment, lithium extraction, and lithium adsorption.

1. Introduction

Lithium source has been paid attention due to the wide applications such as cathode materials for rechargeable batteries, light aircraft alloys, catalyst, and nuclear fusion fuel. Recently, there has been an increasing demand for lithium, owing to the rapid expansion of the worldwide lithium battery market [1–4]. Several methods such as adsorption, solvent extraction, and coprecipitation [5–8] have been studied to extract lithium from seawater, brine, and geothermal water. Among them, the adsorption method to recover lithium from seawater is the most attractive considering that seawater is a vast lithium sources containing about 2.5×10^{14} kg of lithium [9] compared with other reservoir sites although lithium concentration is low (0.17 mg dm^{-3}) in seawater.

Many researchers have investigated on the fabrication of spinel-type lithium manganese oxides (LMOs) such as $LiMn_2O_4$, $Li_{1.33}Mn_{1.67}O_4$, and $Li_{1.6}Mn_{1.6}O_4$ for the recovery of lithium from aqueous solutions [10–16]. LMO shows the noticeable adsorptive properties and especially high selectivity to lithium, including chemical stability with low toxicity, which is suitable to apply in an

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aqueous solution. However, powder-type adsorbent cannot be used directly for the practical application due to the recovery difficulty of adsorbent powder after the use in the aqueous solution. To solve this drawback, many trials have been conducted to evaluate the direct application of adsorbent powder using binders on membranization [17], foaming methods [18,19], and granulation [20], and using reservoir system [21]. These methods still require the improvement for the practical application of adsorbent since the adsorption site on the adsorbent powder can be blocked by the use of binders, and at least two-step processes are required (preparation of adsorbent powder; forming with binder). Larger adsorbent powder particle size is needed for reservoir systems to prevent leakage from the reservoir, and it also has a difficulty associated with flowing aqueous solutions through the reservoir.

In our previous work [22], we reported the preparation of the cylinder-type adsorbent using water glass as a binder due to its good adhesive property. Water glass is an inorganic binder and can be used at high temperature. The reactants (Li_2CO_3 and $MnCO_3$) were mixed with the binder and directly used for forming. The mixing was followed by a heat treatment to produce cylinder-type LMO. The cylinder-type LMO remained stable after the lithium extraction and adsorption processes, although its adsorption capacity was lower (55%) than that of LMO powder due to the blockage of the adsorption sites by the binder.

In this study, we examined the Li^+ adsorption reaction between LMO powder and cylinder-type LMO, and improved the adsorption capacity of cylinder-type LMO by adding Na_2CO_3. Na_2CO_3 was used as an additive due to its thermal stability which suppresses side reactions with the spinel structure formation during the heat treatment, and good solubility in acid solutions, which generates additional internal channels and pores in the structure during the acid treatment. The effect of the additive on the adsorption capacity of cylinder-type LMO was evaluated. Finally, the adsorption capacity of cylinder-type LMOs with/without additive was examined with comparison of a powder-type adsorbent.

2. Experimental

2.1. Preparation of spinel lithium manganese oxide (LMO)

Powder-type LMO (referred to as LMO-powder) was synthesized via a solid state reaction using Li_2CO_3 (99%, Aldrich, USA) and $MnCO_3$ (99.9%, Aldrich, USA) as starting materials. The Li/Mn molar ratio was 1.33/1.67. Prior to the heat treatment, the weighed reactants were well mixed using a ball mill. A 10 g mixture was placed in a ceramic boat and heated in a box furnace at 500 °C for 4 h under air atmosphere.

Water glass (36.8 wt% sodium silicate–H_2O) was used as a binder to prepare the cylinder-type LMO (referred to as LMO-cylinder). The weight ratio of the powder (reactant mixture, Li_2CO_3–$MnCO_3$) to the binder (water glass) was 1.6/1 when tested as an optimum extrusion condition. The reactant mixture and water glass were mixed using a mechanical mixer and extruded into a cylindrical shape 3 mm in diameter and 10 mm long using a mechanical extruder. The resulting cylinder was dried at 60 °C in an oven overnight and then heated in a box furnace at 500 °C for 4 h under air atmosphere. Na_2CO_3 (99%, Aldrich, USA) was used as an additive for the preparation of LMO-cylinder. The amount of Na_2CO_3 was controlled from 2 wt% to 10 wt% in the reactant mixture (Li_2CO_3–$MnCO_3$–Na_2CO_3), and the resulting mixture was formed into the cylindrical shape using the aforementioned procedure.

The crystal structure of the resulting products was determined using an X-ray diffractometer (XRD, D/MAX 2200, Rigaku). The morphology was analyzed using analytical scanning electron microscopy (SEM, Topcon sm-300) with energy dispersive X-ray spectrometry (EDS) that also gave the distribution of the elements in the resulting product. The analyses of the surface area and pore volume were performed using BET and BJH methods with a Tristar II 3020 Surface Area and Porosity Analyzer.

2.2. Batch experiment of Li^+ adsorption on LMO-powder and LMO-cylinders

The prepared LMOs (LMO-powder and LMO-cylinders) were treated using a 0.3 M HCl solution at 25 °C to extract Li^+ from the LMO structure, which yielded the lithium adsorbent. The solution was then filtered using a membrane filter with a 0.1 μm pore size. The filtered LMOs were washed with de-ionized water to rinse away the remaining HCl solution and dried in an oven at 60 °C.

The lithium adsorption capacity of the acid-treated LMOs was investigated in lithium-enriched seawater at 25 °C. LiCl (99%, Aldrich, USA) was used to artificially spike the Li^+ concentration from 1 to 60 mg L^{-1} in the filtered seawater. Adsorption tests were conducted by shaking 1 g of acid-treated LMOs in 2 L of lithium-enriched seawater using a mechanical shaker at 120 rpm and 25 °C until the adsorption reaction reached an equilibrium state. The lithium adsorption capacity (q_e) was calculated by:

$$q_e(mg_{Li}/g_{adsorbent}) = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o and C_e are the initial and final Li concentration (mg L^{-1}), respectively; V is the volume of the solution (L); and m is the mass of applied adsorbent (g). The concentration of ions in the solution was analyzed with an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Optima 7300D, PerkinElmer).

3. Results and discussion

LMO-powder and LMO-cylinder were prepared via a solid state reaction at 500 °C for 4 h and their delithiated products were obtained after the acid treatment using a 0.3 M HCl solution for three days. Both LMO-powder and LMO-cylinder exhibited clear spinel phase of lithium manganese oxide peaks in Fig. 1A. LMO-cylinder showed no crystalline phase resulting from the water glass and by-product, implying that the heating temperature (500 °C) was low enough to prevent the formation of sodium silicate crystalline structures from the water glass and it was not reacted with LMO reactants. The grain size of the LMO-powder, calculated by applying the Scherrer equation, was 67 ± 1 nm, whereas that of the LMO-cylinder was approximately 44 ± 1 nm. The decrease in the grain size might be due to the presence of sodium silicate resulted from the water glass, which could act as a grain growth inhibitor during the heat treatment. The BET surface area of the LMO-powder was 13.9 m^2 g^{-1}, whereas it was 6.8 m^2 g^{-1} for the LMO-cylinder, which can be attributed to the space occupied by the binder in the structure. Prior to the adsorption test, lithium was extracted (>99%) from the LMO structure by shaking the LMO-powder and LMO-cylinder in a 0.3 M HCl solution using a mechanical shaker for three days. The LMO-powder and LMO-cylinder before/after the acid treatment showed nearly identical XRD patterns, whereas the major peaks shifted to slightly higher two-theta values after the lithium extraction. The peak shift before/after the acid treatment is typically observed after acid treatment of LMO structures, and indicates that the lithium extraction proceeded topotactically while the original spinel structure was maintained [10].

Fig. 1B shows the nitrogen adsorption–desorption isotherms of the LMO-cylinder obtained before/after the lithium extraction. A hysteretic loop indicating a type-IV isotherm curve of mesoporous materials was observed. This curve can be obtained from typical mesoporous materials, which exhibit capillary condensation and