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Millimeter-sized spherical ion-sieve foams with hierarchical pore structure for recovery of lithium from seawater

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HIGHLIGHTS

- ▶ Millimeter-sized spherical ion-sieve foams (SIFs) are prepared for Li^+ recovery.
- ▶ SIFs exhibit spinel structure and hierarchical trimodal pore structure.
- ▶ Li^+ adsorption of SIFs in LiOH solution decreases with agar content.
- ▶ Li^+ adsorption efficiency is over 95% even after five adsorption–desorption cycles.
- ▶ Li^+ desorption efficiency is maintained at about 86% after five treatment cycles.

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ABSTRACT

Millimeter-sized spherical ion-sieve foams (SIFs) were prepared from spinel lithium manganese oxide (LMO) via a combined process of foaming, drop-in-oil, and agar gelation to recover the lithium from natural seawater. The spinel structure of the fabricated SIFs was induced by H^+–Li^+ ion exchange after acid treatment, and the SIFs were found to exhibit hierarchical trimodal pore structure. Small and large bimodal mesopores were formed from the acid treatment-induced agar removal, and macropores from the bubble-template. Increasing agar content during the fabrication process led to an increase in the specific surface area and mesopore volume of the SIFs, but a decrease in the macropore volume. The amount of lithium adsorption in the LiOH solution was significantly decreased with increasing agar content during the fabrication process, probably because the SIFs fabricated with lower agar content possessed more open pores, which in turn increased the contact probability with the hierarchical structure developed in the inner parts of the SIFs. The SIFs with the lowest agar content exhibited greatest lithium adsorption capacity in natural seawater of 3.4 mg g^{-1}, and the adsorption and desorption efficiency were almost unaffected even after five adsorption–desorption cycles.

1. Introduction

Lithium is widely used across a variety of industry sectors with rapidly increasing consumption, especially in the lithium-ion battery industry [1,2]. Despite lithium's low marine concentration of 0.17 mg L^{-1}, the lithium reserves in the sea total approximately 2.5×10^{14} kg, which represents a promising source for coastal nations [3,4]. According to research presently being conducted on selective lithium recovery in seawater, inorganic adsorbents with extremely high selectivity and capacity for capturing lithium ions from liquid lithium resources are called lithium ion-sieves (LISs) [4–7]. Their low toxicity, low cost, and high chemical stability make LISs suitable for lithium recovery from seawater. Spinel manganese oxide derived from spinel lithium manganese oxide (LMO) after topotactically extracting lithium from the spinel-structure by acid treatment is the most widely investigated LISs [4,7–9]. Ion-sieve-type spinel LMO has been evaluated as the most appropriate LISs for application to brine and seawater. However, because LISs are normally fabricated in powder form, their utilization in industrial applications has remained limited.

Much research effort has focused on applying LISs to liquid lithium resources for industrial applications. Both Onodera et al. [10] and Sagara et al. [11] injected ion-sieve powder into macroporous beads in order to fabricate granular lithium adsorbents. They summarized the characteristic advantages of granular lithium adsorbents as their ease of packing in a column due to their spherical shape and their excellent selectivity for lithium. However, unfortunately their lithium adsorption performance was relatively low

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compared with the powder form. Afterward, Umeno et al. [12] mixed LMO with dimethylformamide (DMF) solvent including poly(vinyl) alcohol (PVA) binder. After heating the mixture, they dropped it into an aqueous solution through a nozzle to obtain granules with a size range of 2–3 mm. Then, they rinsed the granular materials with plenty of water to dissolve DMF, which was contained in PVA, and thereby fabricated membrane-type lithium adsorbents with micropores. However, this fabrication method suffers high manufacturing cost, copious environmental emissions of harmful substances, and substantial DMF wastewater generated from a preparation process.

The absorbents produced by this fabrication method have significantly less adsorption capacity than ion-sieve powder. Recently, Chung et al. [7] used non-woven fabric and polysulfone to make ion-sieve powder containing a polymeric membrane reservoir for lithium recovery. Complete utilization of the powder characteristics offers a superior capacity to that of other relevant practical methods thus far reported such as artificial seawater $((C_{\mathrm{Li}}^{+}) = 100\ \mathrm{mg\ L^{-1}}$, lithium capacity = 36.1 mg g^{-1}, 24 h). Nevertheless, the method does suffer the disadvantages of the loss of the adsorbent in aqueous solution and the blockage of lithium holes due to the wrapping effect caused by non-woven fabric. Moreover, the method requires the water diffusion rate be increased by applying hydrophilic functional groups to the outer surface of the membrane. Ma et al. [13] reported a method to fabricate the sponge foam-type lithium adsorbent with a specific size (50 mm × 30 mm × 6 mm) by using pitch (e.g., bitumen or resin) binders. The structure of the invented adsorbent was not collapsed or broken by lithium adsorption/desorption. The meso-/macroporous structure of the adsorbent appeared to contribute positively to the adsorption performance. However, compared to the powder-type, foam-type lithium adsorbents showed a significantly low adsorption capacity (brine $(C_{\mathrm{Li}}^{+}) = 234\ \mathrm{mg\ L^{-1}}$, lithium capacity = 1.5 mg g^{-1}, 24 h). The lithium hole was considered to have become clogged by the inclusion of high binders. The biggest drawbacks of the method, as noted by Ma et al., are the numerous environmentally hazardous substances generated in the manufacturing process and the high manufacturing cost.

The critical aspect of the application of lithium adsorbents to liquid lithium resources is retaining the performance of LIS powders – starting materials – over as many cycles as possible. Preserving the lithium adsorption capacity for as long as possible is also important. Research on improving the lithium adsorbent performance has therefore focused on utilizing a binder that can be used for producing adsorbents at very low additive contents and establishing a hierarchical trimodal pore structure that facilitates the formation of a spinel framework, in order to improve the solid-state diffusion of $\mathrm{Li^+}$ and $\mathrm{H^+}$. Recently, we reported on a simple and environmental friendly method for preparing sizable or uniformly sized foam spheres by using aqueous agar solution as the binder [14]. The aqueous agar solution resulted in rapid gelation at low temperatures and gave the fabricated materials a high gelling strength, even at low agar concentrations. In addition, foam spheres with hierarchical trimodal pore structure were fabricated from this method. Hence, it is anticipated that spherical lithium adsorbents of millimeter size, which allows easy installation and recovery, could be produced via the above method. Moreover, the method is considered to be environmental friendly since a biopolymer (i.e., agar) is used as a binder and the manufacturing costs are low due to the simple manufacturing process and inexpensive raw materials. The main purpose of this paper is to fabricate a new type of lithium adsorbent with excellent performance in the recovery of lithium from seawater. To this end, spherical foams with a hierarchical pore structure were fabricated from LIS powders by using agar. Additionally, the physical properties of the lithium adsorbents were assessed and their lithium adsorption capacity was evaluated according to the agar content. Finally, the best lithium adsorbent was determined via preliminary experiments on adsorption capacity, and additional absorption–desorption experiments were conducted with this adsorbent and natural seawater.

2. Materials and methods

2.1. Sample preparation

The material precursor, spinel LMO powders, was obtained by solid-state reaction. In the solid-state reaction, lithium carbonate ($\mathrm{Li_2CO_3}$; Sigma–Aldrich) and manganese carbonate ($\mathrm{MnCO_3}$; Sigma–Aldrich) were used as raw materials. Both $\mathrm{Li_2CO_3}$ and $\mathrm{MnCO_3}$ were mixed at a 1.33:1.67 M ratio and homogenized by ball milling for 1 h [15]. The powder mixture was dried at 80 °C and calcined at 500 °C for 4 h at a heating rate of 3 °C min^{-1}. The product in a powder form is denoted as LMO.

The spherical foams from LMO were prepared by a mechanical foaming method along with drop-in-oil and agar gelation [14]. A slurry of 60 wt.% was prepared by mixing LMO and de-ionized water together. The slurry temperature was maintained at a constant 60 °C. Sodium lauryl sulfate (SLS; Sigma–Aldrich) of 4 mL L^{-1} was added to the slurry, which was then foamed and aqueous agar solution (agar particle size distribution of 1–10 μm, Myung Shin Agar Co., Korea) of different concentrations (i.e., 2, 3, 4 or 6%) was added. This foamed slurry was immediately sucked into a syringe with an inner diameter of 2.4 mm for dripping into a liquid paraffin solution (height = 50 cm and temperature = 5 °C) at a flow-rate of 10 cm^3 min^{-1}. During the foaming and dripping, the slurry temperature was maintained at 60 °C. The resulting gelled spheres were collected from the bottom of the liquid paraffin column, dried at room temperature for a week, and then washed in water/ethanol at 5 °C for 1 h to remove any oil and surfactant from the samples.

The spherical samples were immersed in 0.5 M HCl solution at 25 °C for 5 days and then dried at room temperature for 24 h to extract any $\mathrm{Li^+}$ from the spherical samples that had been produced during the acid treatment. Following the $\mathrm{Li^+}$ extraction, the spheres attained an ion-sieve structure of manganese composite oxide. Lastly, millimeter-sized, spherical ceramic foams with an ion-sieve type structure were prepared for lithium recovery. The resulting LMO and spherical samples obtained after acid treatment were designated as HMO and spherical ion-sieve foams (SIFs)-*x*, respectively, where *x* indicates the added agar mass percentage.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded with a Bruker D8 HRXRD (Germany) X-ray diffractometer using Ni-filtered Cu Ka radiation (λ = 0.154606 nm, 40 kV, 40 mV). The microstructure and morphology of the samples were investigated with a JEOL JSM-6701F field emission scanning electron microscope (FE-SEM, Japan). FE-SEM images of the Au-sputtered samples (whole spheres and cross-section) were taken at an acceleration voltage of 15 kV. Intrusion macropore volumes, open porosities and pore size distributions were recorded by mercury porosimetry using a Micromeritics AutoPore IV 9500 V1.07 (USA) porosimeter. The apparent densities of HMO and LMO and the skeletal density of the spherical samples were measured by a Micromeritics Helium AccuPyc II 1340 pycnometer. The porosities of the spherical samples were calculated with reference to the experimentally measured values (i.e., bulk, apparent, and skeletal density) [16,17]. In addition, nitrogen adsorption–desorption isotherms were obtained by a Micromeritics ASAP 2020 sorptometer at liquid nitrogen (77 K) temperature. The samples were evacuated prior to