



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

Yosep Han<sup>a</sup>, Hyunjung Kim<sup>b,\*</sup>, Jaikoo Park<sup>a,\*</sup>

<sup>a</sup> Department of Natural Resources and Environmental Engineering, Hanyang University, #17 Heangdang-Dong, Seongdong-Gu, Seoul 133-791, Republic of Korea

<sup>b</sup> Department of Mineral Resources and Energy Engineering, Chonbuk National University, 664-14 Duckjin-Dong 1Ga, Deokjin-Gu, Jeonju, Jeonbuk 561-756, Republic of Korea

## HIGHLIGHTS

- ▶ Millimeter-sized spherical ion-sieve foams (SIFs) are prepared for Li<sup>+</sup> recovery.
- ▶ SIFs exhibit spinel structure and hierarchical trimodal pore structure.
- ▶ Li<sup>+</sup> adsorption of SIFs in LiOH solution decreases with agar content.
- ▶ Li<sup>+</sup> adsorption efficiency is over 95% even after five adsorption–desorption cycles.
- ▶ Li<sup>+</sup> 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<sup>+</sup>–Li<sup>+</sup> 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<sup>-1</sup>, and the adsorption and desorption efficiency were almost unaffected even after five adsorption–desorption cycles.

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## 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<sup>-1</sup>, the lithium reserves in the sea total approximately 2.5 × 10<sup>14</sup> 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

\* Corresponding authors. Tel.: +82 63 270 2370; fax: +82 63 270 2366 (H. Kim), tel.: +82 2 2220 0416; fax: +82 2 2296 9724 (J. Park).

E-mail addresses: [kshjkim@jbnu.ac.kr](mailto:kshjkim@jbnu.ac.kr) (H. Kim), [jpark@hanyang.ac.kr](mailto:jpark@hanyang.ac.kr) (J. Park).