



Macroporous flexible polyvinyl alcohol lithium adsorbent foam composite prepared via surfactant blending and cryo-desiccation



Grace M. Nisola^{a,1}, Lawrence A. Limjoco^{a,1}, Eleazer L. Vivas^a, Chosel P. Lawagon^a, Myoung Jun Park^{a,b}, Ho Kyong Shon^b, Neha Mittal^a, In Wook Nah^c, Hern Kim^a, Wook-Jin Chung^{a,*}

^aEnergy and Environment Fusion Technology Center (E²FTC), Department of Energy Science and Technology (DEST), Myongji University, Myongji-ro 116, Nam-dong, Cheoin-gu, Yongin-si, Gyeonggi-do 449-728, Republic of Korea

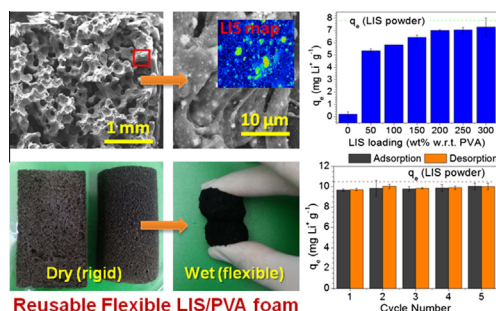
^bCentre for Technology in Water and Wastewater (CTWW), School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), P.O. Box 123, 15 Broadway, NSW 2007, Australia

^cCenter for Energy Convergence, Korea Institute of Science and Technology (KIST), Hwarangno 14-Gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea

HIGHLIGHTS

- Flexible LIS/PVA foams were prepared via surfactant blending and cryo-desiccation.
- Uniform distribution of LIS within the PVA foam network was achieved.
- High porosity, specific surface area, and water absorbency of LIS/PVA foams.
- Comparable adsorption capacity and kinetics of 250 wt% LIS/PVA with LIS powder.
- LIS/PVA are durable and recyclable with consistent performance for long-term use.

GRAPHICAL ABSTRACT



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ABSTRACT

Macroporous polyvinyl alcohol (PVA) foam composites with high loading of uniformly distributed lithium ion sieves (LIS) were successfully fabricated and evaluated for Li⁺ recovery. Surfactant blending combined with cryo-desiccation effectively produced LIS/PVA foams with hierarchical porosity composed of macro- and mesopores. Glutaraldehyde cross-linking rendered the LIS/PVA foams insoluble in water but exhibited high water absorbency and flexibility. Relative to the LIS powder, the foams exhibited minimal reductions in adsorption capacity (q_e) and kinetic properties due to: (1) high total porosity and surface area, (2) hydrophilicity of PVA matrix, and (3) high LIS loading, which promoted particle exposure on the foam surface. These features facilitated easy convective flow of water through the matrix and allowed intimate contact between the Li⁺ feed source and the LIS surface. Thus, LIS/PVA foams with high loadings (200–300 wt%) exhibited meager reductions in q_e (7–13%) and kinetic properties compared to the LIS powder. With LIS loading increase, Li⁺ selectivity of LIS/PVA foams against other cations (i.e. Na⁺, K⁺, Mg²⁺, Ca²⁺) likewise approached that of the LIS powder. While 300 wt% LIS/PVA had low mechanical property, lower LIS loadings of 200- and 250 wt% were highly durable and exhibited no deterioration in adsorption performance and reusability. Among the prepared LIS/PVA, 250 wt% demonstrated the highest adsorption performance and can be repeatedly used for long-term application. The developed LIS/PVA foams are promising Li⁺

* Corresponding author. Tel.: +82 31 330 6687; fax: +82 31 337 2902.

E-mail address: wjc0828@gmail.com (W.-J. Chung).

¹ Co-first authors.

adsorbents for secondary Li⁺ sources; application of these foams via a simple “absorb and squeeze” mechanism could be more practical than the energy-intensive processes like packed bed and membrane systems.
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1. Introduction

The emerging industrial relevance of lithium (Li) has driven interests on its recovery from all viable resources including those in waste batteries, industrial wastewater, coal ash, and seawater [1–5]. However, mining of diluted Li ions (Li⁺) from alternative sources remains a challenge [6–7]. Methods like solvent extraction, ion exchange resins, co-precipitation, adsorption, and membrane process have been explored [5–11]. Among them [8], adsorption by lithium ion sieves (LIS) is the most promising as it can selectively assimilate Li⁺ from a stream containing other more abundant cations [5,10].

The LIS powders are more conveniently handled and reused if immobilized in polymeric matrices or inorganic materials [11–18]. Membranization and granulation have been typically employed for the preparation of LIS composites using various types of polymers as LIS binders. However with these methods, LIS adsorption performances are often compromised due to the unfavorable structural property of the composites and because of the physical obstructions inculcated by the polymer matrix [11–14,17]. Thus, development of more effective LIS composites with minimal performance reduction (i.e. relative to the LIS powder) remains a challenge.

A three-dimensional network of interconnected pores, which is typically exhibited by poriferous foams, could be an interesting structural feature of an LIS composite [19,20]. Apart from its favorable structure, flexible foam adsorbents can be conveniently used via “soak and squeeze” mechanism for Li⁺ uptake and recovery, respectively. This is a great economic advantage over granulated and membrane-type adsorbents, which require energy-intensive pumping systems for the operation of packed bed and membrane modules, respectively [11,17].

However, development of sponge-type LIS composites is largely unexplored in literature. A previous study employed template method wherein poly-urethane (PU) foam was used as a support, on which the LIS adsorbent dispersed in petroleum-derived pitch was deposited [17]. As a coating method, the bulk inert PU template occupied majority of the material volume hence significantly limited the specific loading of the LIS. Moreover, hydrophobic pitch severely impaired the LIS adsorption performance whereas deterioration of the deposited LIS/pitch after repeated use shortened the lifetime of the foam composite.

High LIS loading can be achieved by producing the bulk foam directly from the LIS/polymer mixture, wherein the LIS would be uniformly distributed throughout the foam structure [19]. Foam porosity can be generated through pore-forming agents like inorganic salts, liquid gels, and metal particles [21]. However, the challenge of efficiently leaching out the porogens necessitates more effective methods [19]. Gas-evolving agents have also been used for pore generation but noxious emissions (i.e. CO₂ from calcium carbonate) are considered unfavorable to the environment [22]. On the other hand, surfactant addition with vigorous blending is a convenient technique to prepare macroporous foams. With sufficient surfactant, the surface tension of foam precursor is reduced and introduction of air pockets as macropore templates (via blending) is easily achieved [23,24].

Meanwhile, cryo-desiccation is another facile and environmentally benign technique which has been effectively applied in producing poriferous materials like foams for different applications.

In cryo-desiccation, the sublimation of ice crystals from frozen materials under reduced pressure would generate evacuated regions or void spaces which could contribute to the porosity of the foams [19,25,26].

Thus in the current study, highly porous flexible foams with high LIS loadings (50–300 wt%) were successfully synthesized directly from LIS/polymer binder mixture (Fig. 1) via surfactant blending combined with cryo-desiccation. Delithiated Li_{1.6}Mn_{1.6}O₄ or H_{1.6}Mn_{1.6}O₄ was the selected LIS for convenient literary comparison [5,8,10,11–18]. Meanwhile, polyvinyl alcohol (PVA) was the chosen binder due to its high hydrophilicity, excellent binding ability, chemical resistance, and convenient processability [13,27–29]. Macroporosity was generated by blending the LIS/PVA mixture with a non-ionic surfactant (i.e. Triton X-100) followed shortly by freezing, to preserve the bulky structure of the foam. Subsequent cryo-desiccation conveniently dehydrated the LIS/PVA which resulted in dried highly porous LIS/PVA foams. As PVA readily dissolves in water, the foams were stabilized through acid-catalyzed glutaraldehyde (GA) cross-linking, as reported in numerous studies [27,29,30]. The prepared LIS/PVA foams were evaluated through their Li⁺ adsorption properties (isotherms and kinetic studies), Li⁺ selectivity, and reusability for long-term application.

2. Experimental

2.1. Materials

Lithium manganese dioxide powder (LiMnO₂, >99% trace metal basis, particle size < 1 μm), GA cross-linker (grade II, 25% in H₂O), and PVA polymer (98–99% hydrolyzed, average MW = 85,000–124,000 g mole⁻¹) were purchased from Sigma–Aldrich (Mo., USA). Hydrochloric acid (HCl, RHM 35–37%) and nitric acid (RHM 60% HNO₃) were from Junsei Chemical Co., Ltd. (Japan). Surfactant polyoxyethylene octyl phenyl ether (Triton X-100[®]) was obtained from Acros-Organics (USA) while ethanol (>99.90%) was purchased from Daejung Chemicals, Co., Ltd., (Korea). Lithium hydroxide (LiOH, ≥98%) was from Sigma–Aldrich (Mo., USA) and lithium chloride (LiCl, ≥98%) was from Fluka (Switzerland). All chemicals were used without further purification.

2.2. LIS powder preparation

The LIS was prepared as described in previous studies [5,15]. The LiMnO₂ precursor was ground with mortar and pestle, sieved (No. 200, = 63 μm), and then thermally-treated in air (10 °C min⁻¹ at 450 °C for 4 h) to produce Li_{1.6}Mn_{1.6}O₄. The powder was then delithiated in 0.5 M HCl solution for 24 h (1 g L⁻¹) to obtain H_{1.6}Mn_{1.6}O₄ as the LIS, via topotactic Li⁺/H⁺ ion exchange. The LIS dispersion was vacuum-filtered and then washed repeatedly with deionized (DI) water until neutral pH was achieved. The slurry was dried at 30 °C and the final LIS powder was stored in a desiccator before use. Identity of the LIS was confirmed through X-ray diffraction analysis (40 kV, 30 mA, 0.02 step count⁻¹, Cu K source PANalytical X'pert-Pro, The Netherlands). Result revealed an XRD pattern consistent with those reported in literature (Supplementary Fig. S1) [15,31,32].

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