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Magnetically separable magnetite–lithium manganese oxide nanocomposites as reusable lithium adsorbents in aqueous lithium resources

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HIGHLIGHTS

- Magnetite–lithium manganese oxides (M–LMOs) were prepared for Li^+ adsorption.
- M–LMOs had a spinel structure and contained two crystal phases.
- Li^+ adsorption efficiency was about 86% after 6 adsorption–desorption cycles.
- M–LMOs were conveniently separated from a liquid under an external magnetic field.

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ABSTRACT

Spinel-structured lithium manganese oxides (LMOs) have generated considerable interest as adsorbents for the recovery of Li ions from aqueous Li resources such as brine, seawater, and concentrated seawater. However, practical applications are limited because powdered adsorbents are hard to handle and separate from a liquid. To overcome this problem, magnetically separable magnetite–LMO composite adsorbents (M–LMOs) were prepared by growing magnetite on LMO. The morphologies, crystal structures, chemical compositions, and magnetic properties of the prepared materials were characterized using various analytical techniques. The results confirmed that M–LMO had a spinel structure and contained two crystal phases. Li^+ adsorption experiments were conducted using acid-treated M–LMO (M–HMO). The results confirmed that M–HMO was reusable and selectively adsorbed Li^+ in the presence of Na^+, K^+, and Mg^{2+}; the Li^+ adsorption capacity was 6.84 mg/g in LiCl buffer solution and 1.2 mg/g in concentrated seawater, which is a much harsher condition than brine or seawater. M–HMO was conveniently separated from a liquid under an external magnetic field after Li^+ adsorption. This is significantly different from conventional Li^+ recovery systems such as granulation, foam formation, and membranization. These findings indicate that M–LMO could be used for Li^+ recovery from aqueous Li resources and has good potential for practical applications.

1. Introduction

Interest in Li resources has been increasing because of the rapidly increasing demand for Li as a raw material for Li secondary batteries [1]. Li is present in brines and various minerals such as spodumene, petalite, lepidolite, and amblygonite [2]. Seawater is also a potential source of Li. Although the average concentration of Li^+ in seawater is very low (0.17 mg/L), the total amount of Li^+ in seawater is more than 2.5×10^{14} kg [2,3]. Li can be recovered from seawater directly or after concentration. Concentrated seawater obtained from desalination plants or salt farms is a good potential source of Li^+. In recent years, there has been rapid growth in the construction of desalination plants [4]. Li^+ recovery from concentrated seawater is therefore becoming an important challenge for academic researchers and in industry.

Lithium manganese oxides (LMOs) with the spinel crystal structure are the most effective materials for Li^+ recovery from aqueous Li resources such as seawater, brine, and concentrated seawater. However, powdered adsorbents cannot be used directly in aqueous Li resources because they are difficult to handle and adsorbent recovery from the liquid after Li^+ adsorption is difficult, resulting in loss of adsorbent. Granulation, foam formation, and membranization methods have conventionally been used to deal with

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these drawbacks. Macroporous silica beads [5], macroporous cellulose gel beads [6], and poly(vinyl chloride) (PVC) [7] have been used for granulation of Li adsorbents to an appropriate size. Foam adsorbents have been prepared using various binders such as pitch [8] or agar [9], with LMOs as precursors. These granulated and foam adsorbents are used in column systems for Li^+ recovery; this method has high energy consumption and a high pressure is needed, leading to adsorbent loss. Other research groups have studied membrane-type Li-adsorbing systems as alternatives to column systems. Membrane-type adsorbents have been prepared by a solvent exchange method using PVC as a binder [10]. Flat sheet [11] and polymeric reservoir "tea bag" configurations [12] have been studied. These membrane-type adsorbents are suitable for Li^+ recovery from aqueous Li resources because they can be used in continuous-operation systems, but operation of the pressurized flow component of the membrane system consumes energy [12]. The manufacturing costs are high, and a considerable amount of wastewater containing substances such as *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide [9] is generated. In addition, coverage of the adsorbent surface by polymers decreases the number of active sites for Li^+ adsorption.

In this study, we investigated a magnetic separation method, using magnetic particles, as an alternative to conventional Li^+ recovery systems. Magnetic separation is an effective and simple method for separating particles from a liquid or other fluid. The magnetic particles can be easily separated from solution by a magnetic field and the separated particles can be reused after removal of the adsorbed substance. This method has the advantages of nontoxicity, low cost, and facile synthesis. Magnetic particles are therefore widely used in various fields such as catalysis [13,14], water purification [15–17], and biomedical applications [18–20]. However, magnetic separation in Li^+ recovery systems is in its nascent stage and further investigation is necessary to enable the replacement of conventional Li^+ recovery systems for aqueous Li resources.

A magnetically separable and reusable adsorbent was prepared by growing magnetite (Fe_3O_4) on LMOs with various Li precursor contents, and used for Li^+ recovery. The morphologies, crystal structures, chemical compositions, and magnetic properties of the prepared magnetite–LMO (M–LMO) composite adsorbents were examined using various analytical techniques. The Li^+ adsorption capacities of the composites were determined in LiCl buffer solution. Finally, the best composite adsorbent was evaluated for reusability, adsorption selectivity, and Li^+ adsorption from concentrated seawater.

2. Experimental

2.1. Materials

Manganese sulfate monohydrate ($MnSO_4{\cdot}H_2O$, Daejung Chemicals & Metals), lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, Junsei), hydrogen peroxide (H_2O_2, 30%, Junsei), iron(II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99%, Sigma–Aldrich), sodium hydroxide pellets (NaOH, Daejung Chemicals & Metals), sodium acetate anhydrous (Sigma–Aldrich), hydrochloric acid (HCl, 35%, Daejung Chemicals & Metals), and potassium permanganate ($KMnO_4$, Junsei) were used as received, without further purification. Highly deionized water (18 MΩ/cm) was used in all experiments.

2.2. Synthesis

2.2.1. Preparation of spinel LMO

LMO with the spinel structure was synthesized by a hydrothermal method, using a modified version of a previously reported method [21]. The Li precursor solutions were prepared by dissolving various amounts of $LiOH{\cdot}H_2O$ and 1.2 M H_2O_2 in deionized water. The LiOH precursor solution (50 mL) was added dropwise to a 0.4 M $MnSO_4{\cdot}H_2O$ solution (50 mL). The mixture was stirred with a magnetic stirrer for 2 h. The resulting mixture was poured into a Teflon-lined stainless-steel autoclave and crystallized at 110 °C for 8 h. The product was filtered and washed several times with deionized water. The obtained precipitate was dried at 60 °C for at least 12 h and calcined at 400 °C for 4 h. The LiOH precursor concentration was varied from 2.0 to 3.0 M to obtain LMOs with various Li/Mn ratios (denoted by LMO-2.0, LMO-2.5, and LMO-3.0).

2.2.2. Preparation of M–LMO composites

The composites were synthesized by growing magnetite crystals on the LMO surface. $FeSO_4{\cdot}7H_2O$ (1.6 g) and sodium acetate (3.0 g) were dissolved in deionized and deoxygenated water in a N_2 atmosphere. Then 40% NaOH (3 mL) was added dropwise, with magnetic stirring. The mixture was stirred for 30 min to form a homogeneous $Fe(OH)_2$ solution. An LMO suspension, which was prepared by dispersing the LMO (0.5 g) in deionized water (20 mL) was added to the $Fe(OH)_2$ solution. The mixture was magnetically stirred in a N_2 atmosphere at room temperature for 1 h. The mixture was transferred to a Teflon-lined stainless-steel autoclave and reacted at 200 °C for 12 h. The products were separated using a magnet and washed with deionized water. The purification was repeated several times. After purification, the powders were dried at 60 °C for 12 h. M–LMOs prepared from different LMO precursors were denoted by M–LMO-2.0, M–LMO-2.5, and M–LMO-3.0.

2.3. Characterization

The LMO and M–LMO crystal structures were examined using X-ray diffraction (XRD) at room temperature, with a Bruker New D8 Advance X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å, 40 kV, 40 mA), with scanning from 10° to 80° at 10°/s. The average crystal diameter was calculated using the Debye–Scherrer formula, $D = K\lambda/\beta\cos\theta$, where D is the crystallite size, K is a constant related to the crystal shape, and usually assumed to be 0.89, λ is the wavelength of the X-ray radiation, β is the peak width (full width at half maximum) in radians, and θ is the diffraction angle. The morphologies and crystal structures were investigated using high-resolution transmission electron microscopy (HR-TEM), with a JEOL JEM-3000F instrument, at an accelerating voltage of 300 kV. N_2 adsorption–desorption isotherms were measured using an ASAP2010 instrument (Micromeritics). The specific surface areas of the samples were calculated, using the multiple-point Brunauer–Emmett–Teller method, from the desorption branch of the isotherm. The magnetic properties of the M–LMOs were investigated by vibrating sample magnetometry (VSM), using the dried powders, at room temperature, with a magnetic field in the range ±10 kOe. The sample compositions were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Varian 730ES). The mean oxidation number of Mn (Z_{Mn}) was estimated from the available oxygen, determined by redox titration using $KMnO_4$ solution. X-ray photoelectron spectroscopy (XPS) was performed to determine the electronic and chemical states, using a Kratos Axis-His instrument with monochromatic Mg K_α radiation as the X-ray source.

2.4. Characterization of adsorption behavior

Li^+ adsorption equilibrium experiments were conducted by stirring acid-treated LMO (HMO) or M–LMO (M–HMO) samples (100 mg) in 0.01 M LiCl buffer solution (100 mL) for 72 h at room