



Preparation of titanium-base lithium ionic sieve with sodium persulfate as eluent and its performance



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HIGHLIGHTS

- Li_2TiO_3 eluted with 0.8 mol/L $\text{Na}_2\text{S}_2\text{O}_8$ had a better application performance.
- The lithium adsorption process followed the pseudo-second-order kinetics mode.
- Cations like Na^+ , K^+ and Mg^{2+} had a little effect on the adsorption performance.

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ABSTRACT

Lithium ionic sieve precursor Li_2TiO_3 was synthesized by a solid-phase reaction with Li_2CO_3 and TiO_2 as the raw materials. The effect of the roasting temperature, the roasting time and the molar ratio of $\text{Li}_2\text{CO}_3/\text{TiO}_2$ on the synthesis of precursor were investigated respectively. The precursor was eluted with 0.8 mol/L sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), the lithium adsorption properties after elution and its lithium uptakes in different aqueous solutions containing lithium were investigated respectively. The structure and surface morphology of the samples were characterized by XRD (X-ray diffraction) and SEM (scanning electron microscope). The results indicated that the optimal synthesis conditions of monoclinic lithium metatitanate (Li_2TiO_3) were $n(\text{Li}_2\text{CO}_3/\text{TiO}_2) = 1.05$, baking temperature of 850 °C for 5 h with a heating rate of 4 °C/min; the precursor eluted with 0.8 mol/L $\text{Na}_2\text{S}_2\text{O}_8$ showed better performance, and its adsorption process followed the pseudo-second-order kinetics mode; coexisting metal ions such as Na^+ , K^+ and Mg^{2+} had a little effect on the adsorption performance.

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1. Introduction

Lithium and its compounds are widely used in manufactured glass, ceramics, greases, batteries, refrigerants, chemical reagents and other industries, which are of great significance in the development of national economy. Global lithium reservation is about 14 million tons (U.S. Geological Survey, published January 2017 annual report), the majority (about 70%–80%) is conserved in salt lake brine and the rest is mainly contained in lithium ore. In recent years, more and more researches turn their attention to the seawater containing about 2600 billion tons lithium, which is about 15,000 times of the amount on land. The following methods are

used to realize the lithium extraction from brine [1]: precipitation, solvent extraction, selective membrane separation, adsorption and ion exchange, and so on. Among of them, the method of adsorption and ion exchange relying on carrier (like adsorbent and ionic sieve) has received more and more takes [2,3] because of its good recycling and high selectivity for the target ion, especially the application in low grade brine or bitter.

The common lithium ionic sieves include manganese-base lithium ionic sieve (Mn-LIS) [4–9], titanium-base lithium ionic sieve (Ti-LIS) [10,11] and their derivative type [12,13]. Among of them, Mn-LIS is focused on earlier than others. The synthesis, characterization and application of Mn-LIS have been carried out plentifully, and several advantages like high selectivity for lithium, good Li^+ uptake capacity and recycled usability have been recognized. However, concerns on long-term recycling of Mn-LIS have been raised because the appearance of Mn^{2+} during elution accounts for the dissolution of part structural framework [14,15].

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Ti-LIS and the derivative type gradually spring up aiming to overcome above insufficient. Comparing to manganese-base lithium ionic sieve, titanium-base lithium ionic sieve possesses superiorities in the lower loss of skeleton element, better periodicity and more stable structure [16]. Chitrakar et al. [11] obtained the ionic sieve H_2TiO_3 by eluting the precursor Li_2TiO_3 (LTO) with hydrochloric acid, and its uptake of lithium was 4.7 mmol/g at pH 6.5 and the distribution coefficient of lithium was higher than that of other ions in the brine; Yan et al. [17] obtained the adsorbent by roasting the mixture of rutile titanium and lithium, and its exchange capacity came up to 29.15 mg/g; Sinha et al. [18] acquired the lithium ionic sieve precursor LTO via the solid-state reaction and got the lattice parameters of LTO; Zhang et al. [19] prepared the precursor LTO using solid-state method, then the adsorbent was obtained after eluting with 0.1 mol/L hydrochloric acid at 60 °C, and the extraction ratio of lithium from Li_2TiO_3 and the loss ratio of titanium were 98.86% and 0.1%, respectively. Lawagon et al. [20] synthesized LTO by mixed TiO_2 and Li_2CO_3 , then it was dispersed in 0.2 mol/L HCl solution at 30 °C for 24 h, and its adsorptive capacity of Li^+ could reach 94.5 mg/g in aqueous solution with higher Li^+ levels. However, the defect of titanium lithium ionic sieve was that it has a slow reaction rate [11,16,21,22] during the process of elution and adsorption.

The lithium ionic sieve can be acquired after elution with eluent such as hydrochloric acid [8,10,23], nitric acid [24], sulfuric acid [4], peroxydisulfate [25] etc. The extraction ratio of Li^+ as well as the loss amounts of manganese or titanium enhances with the increase of concentration of HCl, HNO_3 and H_2SO_4 while eluting the precursor or the product after adsorption. In other words, the structure of adsorbent is more easily damaged along with the concentration of eluent (HCl, HNO_3 and H_2SO_4) increasing. The existing researches show that the adsorption capacity is relatively stable and the loss amount of manganese is decreased when the precursor is eluted by peroxydisulfate ($(NH_4)_2S_2O_8$, $K_2S_2O_8$, $Na_2S_2O_8$) [26], and the elution-adsorption effect and cycle performance of peroxydisulfate as eluent are better than those of the acid agent as eluent. In addition, to some extent $Na_2S_2O_8$ as eluent could alleviate the dynamic shortcoming of monoclinic Ti-base lithium ionic sieve [22].

Researches on the preparation of titanium-base lithium ionic sieve eluted by peroxydisulfate are rarely reported. In this study, the precursor was prepared by solid-state reaction between the anhydrous Li_2CO_3 and TiO_2 , and it was eluted with 0.8 mol/L $Na_2S_2O_8$ which is the optimal concentration through pre-research, then the process of adsorption in the Li-containing aqueous solution and the effect of main coexisting cations (such as Na^+ , K^+ and Mg^{2+}) were investigated, respectively.

2. Experimental

2.1. Preparation of the precursor of lithium ionic sieve

Raw materials deployed in this study were analytical grade without further purification. Lithium ionic sieve precursor Li_2TiO_3 was synthesized by a solid-phase reaction between titanium dioxide (TiO_2) and anhydrous lithium carbonate (Li_2CO_3). The mixture was stirred at room temperature for 3 h with ethyl alcohol as dispersant. After stirring, the suspension was treated with ultrasonic for 10 min to obtain a homogeneous product. Then it was filtrated and the residue was dried in a drying box. After above pretreatment, the precursor LTO was obtained by roasting the residue at a high temperature with muffle in a heating procedure (4 °C/min). All the effect of the roasting temperature (700–950 °C), roasting time (4–6 h) and the molar ratios of Li_2CO_3/TiO_2 (1.01–1.07) on the synthesis of LTO were investigated, respectively.

2.2. Elution/adsorption performance

In this experiment, the performance of elution/adsorption was investigated under three cycles. 4–4.5 g of precursor Li_2TiO_3 was immersed in 0.8 mol/L $Na_2S_2O_8$ solution (400 mL) at 60 °C and stirred for 6 h. Then the product after elution was filtrated and washed with deionized water until pH near to 7, and then dried at 80 °C for 5 h. The filtered and dried samples may called lithium ionic sieve (H_2TiO_3) (abbreviated as Na-TO). After adding the pre-weighed Na-TO into 400 mL 0.1 mol/L $LiCl + LiOH$ aqueous solution (2.12 g/L $LiCl$ and 1.20 g/L $LiOH$) or a simulated salt lake brine at room temperature for 6 h, the product after the adsorption can be named $(Li)_2TiO_3$ (abbreviated as (Li)-TO). According to the cationic composition (Table 1) of Dong Taijinaier salt lake brine, the simulated salt lake brine were prepared by dissolving certain mass of reagents ($LiCl$, K_2SO_4 , $NaCl$ and $MgCl_2 \cdot 6H_2O$) in deionized water.

The samples both in elution and adsorption process were taken at 5, 10, 15, 30, 60, 120, 180, 240, 300, 360 min and filtered with a 0.22 μm syringe filters, then measured with AAS. Looping the product with $Na_2S_2O_8$ solution (300 mL, 300 mL) and then Li-containing solution (300 mL, 300 mL) for another two times.

The extraction amount of lithium or the loss amount of titanium was calculated according to the following equation [27]:

$$q = \frac{C \times V}{m} \quad (1)$$

where q is the lithium extraction amount (or the loss amount of titanium) (mg/g); V is the volume of the eluent (L); C is the concentration of lithium (or titanium) in eluate after eluting with t time (mg/L); m is the mass of the precursor (or product after adsorption) (g).

In the process of adsorption, the concentration of lithium in the filtered supernate was measured after 6 h. Then, the Li^+ uptake of the sample was calculated according to the following equation [27]:

$$Q = \frac{(C_0 - C_t) \times V'}{m'} \quad (2)$$

where Q is the adsorption capacity (mg/g); C_0 is the initial concentration of lithium in the solution (mg/L); C_t is the concentration of lithium in the solution after adsorbing t time (mg/L); V' is the volume of the test solution (L); and m' is the mass of lithium ionic sieve (g).

2.3. Separation coefficient

The separation coefficient is identified as the degree of separation of the two substances by a unit separation operation or a separation process, which is equal to the concentration ratio of one substance in two phases divided by the concentration ratio of another substance in the same two phases. The separation coefficient α_M^{Li} reflects the separation between Li and other metal element M in the solution, and α_M^{Li} can be expressed as the following equation [17]:

$$\alpha_M^{Li} = \frac{Q_{Li}/C_{Li}}{Q_M/C_M} \quad (3)$$

where α_M^{Li} is the separation coefficient of lithium and other metal element M; Q_{Li} and Q_M are the adsorption capacity of lithium and other metal ions (mg/g); C_{Li} and C_M are the equilibrium concentrations of lithium and other metal ions in solution after adsorption (mg/L).

Table 1
The cationic composition of simulated Dong Taijinaier salt lake brine [1].

Constituent	K^+	Na^+	Mg^{2+}	Li^+
Concentration (mg/L)	3793	117030	5640	1950

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