



Lithium ion sieve synthesized via an improved solid state method and adsorption performance for West Taijinar Salt Lake brine

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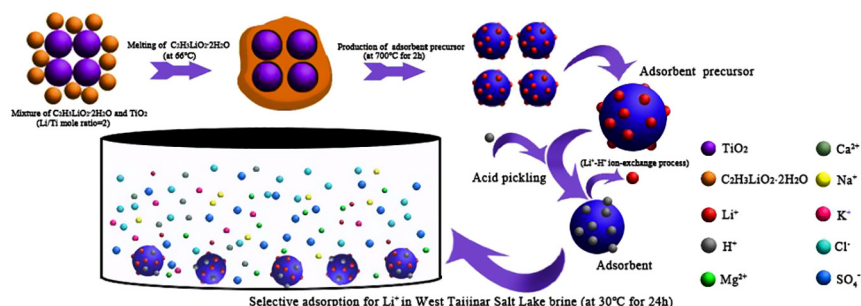


HIGHLIGHTS

- $C_2H_3LiO_2 \cdot 2H_2O$ and TiO_2 were firstly applied to synthesize lithium adsorbent via solid state method.
- Reaction mechanism between $C_2H_3LiO_2 \cdot 2H_2O$ and TiO_2 was analyzed.
- Separation factor α (Li/Mg) in West Taijinar Lake reaches 5441.17.
- Adsorption uptake remains 24.5 mg/g after 5 cycles in West Taijinar Salt Lake brine.

GRAPHICAL ABSTRACT

$C_2H_3LiO_2 \cdot 2H_2O$ was firstly used as the lithium resource to synthesize precursor Li_2TiO_3 . Melting of $C_2H_3LiO_2 \cdot 2H_2O$ (at 66 °C) during the early calcination stage can form liquid–solid phase and remarkably improve mixing of $C_2H_3LiO_2 \cdot 2H_2O$ and TiO_2 . Besides, huge heat and gases released during the reaction of dehydrated $C_2H_3LiO_2 \cdot 2H_2O$ and TiO_2 (between 380 °C and 515 °C) accelerates the nucleation process and effectively inhibited agglomeration, which leads to a smaller particle size of Li_2TiO_3 (~70 nm). Subsequently, Adsorption rate constant of obtained lithium ion sieve H_2TiO_3 reaches 0.0508 g/(mg·h). Separation factor α (Li/Mg) reaches 5441.17, and lithium ion uptake of synthesized H_2TiO_3 could remain around 24.5 mg/g after five adsorption–desorption cycles, meaning better adsorption selectivity and stability of lithium ion for West Taijinar Salt Lake brine.



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ABSTRACT

Monoclinic β - Li_2TiO_3 (LTO) is regarded as a lithium adsorbent precursor. In order to inhibit agglomeration during solid state reaction, $C_2H_3LiO_2 \cdot 2H_2O$ instead of Li_2CO_3 was firstly used as the lithium resource to synthesize LTO. Lithium ion sieve H_2TiO_3 (HTO) was then obtained by acid treatment of LTO. Physicochemical properties of obtained LTO and HTO were characterized via powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and particle size distribution analysis (PSD). Lithium adsorption selectivity and stability of prepared HTO for West Taijinar Salt Lake were investigated. Solid state reaction mechanism of $C_2H_3LiO_2 \cdot 2H_2O$ and TiO_2 was investigated by TG-DTA analysis. Results show that melting of $C_2H_3LiO_2 \cdot 2H_2O$ (at 64.5 °C) during the early calcination stage could form liquid–solid phase and remarkably improve mixing of $C_2H_3LiO_2 \cdot 2H_2O$ and TiO_2 . Compared to Li_2CO_3 used as the lithium resource, huge heat and gases released during the reaction of dehydrated $C_2H_3LiO_2 \cdot 2H_2O$ and TiO_2 (between 380 °C and 515 °C) accelerate the nucleation process and effectively inhibits agglomeration, which leads to a smaller particle size (~70 nm). It is shown that lithium uptake and adsorption rate were improved because of easier mass transfer during the ion-exchange process. Lithium adsorption behavior could be well described by the Langmuir isotherm and pseudo-second-order kinetic model. Separation factor α (Li/Mg) of obtained HTO in West Taijinar Salt Lake brine reached 5441.17, meaning

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remarkable lithium adsorption selectivity in real lake brine. Besides, adsorption uptake remained 24.5 mg/g after 5 cycles in West Taijinar Salt Lake brine, which indicates obtained HTO has good stability.

1. Introduction

Lithium and its compounds have been widely applied in industrial fields such as glass and ceramics, medicine, aerospace and batteries [1,2]. Especially, the development of electronic vehicles (EVs) places much more importance on lithium rechargeable batteries because of high power and energy density [3,4].

Lithium is mainly in spodumene, sea and salt lake brine, during which brine occupies nearly 66% of total deposits in the world [5]. At present, methods for lithium recovery from salt lake brine or sea are mainly based on co-precipitation [6], evaporative-crystallization [7], solvent-extraction [8] and ion-exchange adsorption [9]. Co-precipitation and evaporative-crystallization have been reported for practical application. However, they are only suitable for salt lake brine with low Mg/Li ratio [10]. Solvent-extraction could be used for low-grade salt lake brine. However, excessive reagents used during operation pose a great threat to environment [11]. With high lithium selectivity, ion-exchange adsorption has become a promising candidate for lithium recovery from salt lake brine because of efficient selectivity and environmental protection [12,13]. It is critical for adsorption technology to develop lithium adsorbents with high selectivity and stability.

Reports about Lithium adsorption from salt lake brine were mainly focused on ion-exchange resin, aluminum salt, manganese-based and titanium-based lithium ion sieves (LISs). Ion-exchange resin exhibits a high lithium selectivity with relatively low lithium uptake (< 0.3 mg/g) [14]. Aluminum salt adsorbent has improved lithium uptake of 2–3 mg/g with a low adsorption rate [15]. Manganese-based LISs [16] have high lithium uptake (39 mg/g), however, disproportionation reaction during pickling results in lattice distortion and dissolution of manganese, which undermines cycle performance [17,18]. Titanium-based LISs (H_2TiO_3) have remarkable advantages because of high stability and theoretical lithium uptake.

H_2TiO_3 (HTO) was derived from precursor Li_2TiO_3 (LTO) by pickling procedure. Therefore, in order to obtain HTO with high adsorption performance, it is the key to develop high-quality precursor LTO. LTO was mainly synthesized by hydrothermal synthesis, sol-gel method and solid-state reaction [19–27]. Hydrothermal synthesis requires high temperature and pressure with a long period of time [28]. Sol-gel method involves controlled pH and temperature using chelating agents [29]. With the requirement of simple mechanical mixing and calcination, solid-state reaction is more promising for simple practical production process and environmental protection. Shi et al. [20] prepared LTO at 850 °C for 24 h using Li_2CO_3 and TiO_2 as raw materials and the adsorption capacity came to 28.63 mg/g in 87.5 mg/L LiCl solution. Chitrakar et al. [27] synthesized LTO at 700 °C for 4 h with the same materials and applied the synthesized HTO in pH-adjusted brine lake. The adsorbent exhibited lithium uptake of 32 mg/g. Lawagon et al. [24] synthesized LTO according to Chitrakar's synthesis conditions and comprehensively investigated adsorption behavior of HTO. Equilibrium lithium uptake of obtained HTO reached 33.67 mg/g in 70 mg/L Li^+ solution. Zhou et al. [23,25,26] concentrated on LTO synthesized with $\text{LiOH}\cdot\text{H}_2\text{O}$ and TiO_2 . Under the optimized synthesis conditions (at 650 °C for 5 h), adsorption uptake of obtained HTO reached 57.8 mg/g in 4 g/L LiOH solution at 60 °C [26].

Compared with hydrothermal synthesis and sol-gel method, HTO obtained via solid-state reaction exhibits relatively lower lithium capacity [22]. Using Li_2CO_3 or $\text{LiOH}\cdot\text{H}_2\text{O}$ as the lithium resource, high calcination temperature or a long reaction time needed leads to agglomeration and sintering, which tremendously affects adsorption capacity. In this work, an improved solid-state method was firstly

proposed to reduce agglomeration during solid-state reaction and improve lithium uptake of HTO. Dihydrate lithium acetate ($\text{C}_2\text{H}_3\text{LiO}_2\cdot 2\text{H}_2\text{O}$) was used to synthesize LTO via solid-state reaction and the synthesis mechanism was investigated by TG-DTA analysis, which has not been reported. Besides, a review of references shows that adsorption performance of HTO was mainly evaluated in simulated LiCl solution or LiOH solution. Few literatures focus on adsorption performance of synthesized HTO in real salt lake brine. Reaction conditions such as calcination temperature and time were studied to optimize synthesis process. To make comparison, LTO was synthesized using Li_2CO_3 as the lithium resource according to Lawagon's method [24]. Pickling performance and adsorption property of obtained LTO using two different lithium resource were investigated. Physicochemical properties of obtained LTO and HTO were characterized via powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and particle size distribution analysis (PSD). Selectivity and stability of synthesized HTO using $\text{C}_2\text{H}_3\text{LiO}_2\cdot 2\text{H}_2\text{O}$ as the lithium resource were examined in West Taijinar Salt Lake brine to evaluate its practical application performance.

2. Experimental

2.1. Materials and reagents

Titanium dioxide (TiO_2 , AR, 99.0 wt%) from Sinopharm Chemical Reagent Co., Ltd (China), dihydrate lithium acetate ($\text{C}_2\text{H}_3\text{LiO}_2\cdot 2\text{H}_2\text{O}$, AR, 99.0 wt%) from Jinhua Guangzhou Da Chemical Reagent Co., Ltd (China) and lithium carbonate (Li_2CO_3 , AR, 97.0 wt%) from Xilong Chemical Co., Ltd (China) were used to synthesize LTO. Anhydrous alcohol ($\text{C}_2\text{H}_5\text{OH}$, AR, 99.7 wt%) from Wuxi City Yasheng Chemical Co., Ltd (China) was used as dispersant. Lithium chloride hydrate (LiCl , AR, 97.0 wt%) from Guangdong Guanghua Technology Co., Ltd (China), ammonium chloride (NH_4Cl , AR, 99.5 wt%) from Xilong Chemical Co., Ltd (China) and ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$, AR, 25.0–28.0 wt%) from Shanghai Ling Feng Chemical Reagent Co., Ltd (China) were used for the preparation of simulated Li^+ solution. Hydrochloric acid (HCl, AR, 36.0–38.0 wt%) and sulphuric acid (H_2SO_4 , AR, 95.0–98.0 wt%) from Shanghai Lingfeng Chemical Reagent Co., Ltd (China) were used for protonation and acid digestion of samples, respectively.

2.2. Preparation of lithium ion sieve

2.2.1. Preparation of precursor LTO

$\text{C}_2\text{H}_3\text{LiO}_2\cdot 2\text{H}_2\text{O}$ and TiO_2 according to the stoichiometric molar ratio $n(\text{Li}/\text{Ti}) = 2:1$ were milled and blent with anhydrous alcohol then dried at 40 °C. Dried mixture was calcined at the desired temperature for a period of time at a heating rate of 5 °C/min, before which the mixture was previously treated at 66 °C for 1 h to ensure molten $\text{C}_2\text{H}_3\text{LiO}_2\cdot 2\text{H}_2\text{O}$ was mixed up with TiO_2 homogeneously and spontaneously. Obtained precursor (named LTO-1) was cooled to room temperature.

LTO synthesized using TiO_2 and Li_2CO_3 as raw materials was named LTO-2 according to the early report ($n(\text{Li}/\text{Ti}) = 2:1$, at 700 °C for 4 h) [24].

2.2.2. Preparation of lithium ion sieve HTO

1.8 g LTO-1 or LTO-2 was then treated by 200 mL pickling solution (with certain concentration) at 70 °C for 8 h, followed by filtering, washing and drying to obtain HTO-1 or HTO-2, respectively.

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