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A novel study on preparation of H_2TiO_3–lithium adsorbent with titanyl sulfate as titanium source by inorganic precipitation–peptization method

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A peroxy lithium titanate sol was prepared with low-cost and easily available titanyl sulfate as the titanium source, lithium acetate as the lithium source, and aquae hydrogenii dioxidi as the complexing agent using an inorganic precipitation–peptization method. The sol system was aged, centrifugal-washed, dried and calcined to obtain a pure precursor, Li_2TiO_3, followed by pickling with hydrochloric acid to obtain the H_2TiO_3–lithium adsorbent. The effects of aging time and calcination temperature on the target product were investigated. The results indicate that the sol-system is stable, which is beneficial for loading on a suitable carrier, such as ceramic foams. Centrifugal-washing, instead of vacuum filtration-washing, is conducive to product formation. The most suitable aging time of precursor sol is 24 h and the appropriate calcination temperature is 750 °C. The lithium drawn-out ratio of samples synthesized in this condition reaches 89.50% after pickling with 0.2 M hydrochloric acid for 8 h at 70 °C. Moreover, the Li^+ uptake of the adsorbent (adsorption capacity) reaches 29.96 mg g^{-1} and 33.35 mg g^{-1} when the adsorption time is 1 h and 8 h, respectively.

1 Introduction

Lithium plays an increasingly important role in energy, air conditioning, metallurgy aerospace, etc.[1] With the development of electronic information technology, numerous studies on efficient chemical batteries,[2–5] particularly lithium ion batteries, have been reported. The demand for lithium cannot be met if it is only extracted from solid ore; thus, there is an urgent need to develop methods to extract lithium from liquid ore, such as sea and salt-lake brine, which contain an abundance of lithium. However, traditional precipitation, calcination leaching, carbonization, solvent extraction and salting methods[4–7] are not suitable for lithium extraction from sea and salt-lake brine that contain low lithium concentrations. The use of lithium ionic-sieves,[1,8,9] which is a new approach to address the above-mentioned problems, have increasingly attracted the attention of researchers because of their various remarkable advantages, such as their reduced dissolution rate and stable structure.

The most frequently used titanium–lithium ionic-sieve precursors are Li_2TiO_3 and $Li_4Ti_5O_{12}$. To prepare them, several synthetic techniques, including solid-state reaction, hydrolysis route, sol–gel process and molten-salt microwave-assisted, have been reported.[1,8,10–22] However, it is difficult to use powdery Li_2TiO_3 in engineering because it suffers from the separation of

small solid particles from liquid, washing and regeneration. Ceramic foams are currently widely used in filters, catalyst support, construction, bone scaffold materials, etc.[23–25] due to their high permeability, porosity and specific surface. To solve the problems mentioned above, loading Li_2TiO_3 on ceramic foams can help realize adsorption, elution and regeneration in an ion exchange column.

In our previous studies,[26,27] Li_2TiO_3 was prepared and loaded on ceramic foams via the sol–gel process. However, tetrabutyl titanate, which was employed as a titanium source, is expensive and readily hydrolysed; thus, it is not suitable for industrial applications. Therefore, it is urgent to consider the use of cheap and easily available raw materials. In order to effectively load Li_2TiO_3 on the matrix, a stable sol system with good dispersity is absolutely necessary. For an inorganic substance, the precipitation–peptization approach is an effective way to achieve this purpose. Generally, in this process, the inorganic substance is first hydrolyzed to obtain the fresh precipitate by controlling pH, followed by filtering, washing and beating the filter cake in deionized water to obtain a uniform suspension. Then, the peptizing agent is added to obtain the stable sol-like mixture. Numerous studies on the preparation of the stable sol-like mixture are available in the literature. Anatase TiO_2 colloids, derived from the peptization of TiO_2 precipitates with trifluoroacetic acid, was prepared by Yuan et al.[28] Li et al. obtained a VO_2 sol in air under room temperature using vanadium sulfate as a vanadium source, ammonia as a precipitating agent, and hydrogen peroxide as an initiating agent via inorganic precipitation–peptization method.[29] ZnS phosphor sols doped with

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copper ion were synthesized by the peptization process of sulfide–citrate complex precipitates.[30] Furthermore, $LaPO_4$–ZrO_2 nanocomposites were also successfully developed with a wet chemical synthetic approach involving precipitation–peptization mechanisms.[31] However, to the best of our knowledge, reports regarding the preparation of Li_2TiO_3 by the precipitation–peptization method are rare.

In this study, a stable sol-like system was prepared with lithium acetate as the lithium source, cheap and easily available titanyl sulfate as the titanium source, and aquae hydrogenii dioxidi as the complexing and peptizing agent,[29] which is helpful for loading on a suitable carrier.

2 Experimental

2.1 Preparation of lithium titanate sol

All chemicals were used without any further purification. Titanyl sulfate (CP, Tianjin Guangfu Fine Chemical Research Institution, China) was accurately weighed (8.8 g) and a known volume of deionized water (200 mL, RO pure water), which was obtained from an ultra-pure water machine (UKP-1-100L, Sichuan Youpu Ultra-pure Technology Co., Ltd., China) was added. The mixture was treated in a water bath at 60 °C by continuous stirring to prepare a transparent solution (0.2 mol L^{-1}). Lithium acetate (CP, Shandong Siya Chemical Reagent Co., Ltd., China) was accurately weighed (6.6 g) and the same volume of deionized water (200 mL) was added. The mixture was also treated at 60 °C by uninterrupted stirring to obtain a transparent solution. Concentrated ammonia (10 mL, AR, Chengdu Jinshan Chemical Reagent Co., Ltd., China) was added into the titanyl sulfate solution, which was cooled in advance slowly (about one drop per second) under strong magnetic stirring to produce a white precipitate, during which the pH of the system was regulated at 8–9. Then, the precipitate containing slurry was centrifugal-washed, and similar steps were repeated until sulfate ions were undetectable in the filtrate. The sediment that was eventually centrifuged was diluted with deionized water to obtain a white paste, followed by continuous stirring at room temperature. Then, the CH_3COOLi solution, which was cooled in advance, was slowly poured onto the white paste (about one dropper every ten seconds using a glass dropper with a rubber head) with continuous stirring to ensure even mixing, achieving a Li/Ti molar ratio of 2 : 1. Finally, under uninterrupted stirring, 30% H_2O_2 (22 mL, AR, Chengdu Jinshan Chemical Reagent Co., Ltd., China) solution was slowly poured into the above mixture (about one drop per second) to adjust the Ti^{4+} : H_2O_2 molar ratio to 1 : 4 to peptize the precipitate.

2.2 Preparation and adsorption performance of H_2TiO_3–lithium ion adsorbent

The precursor sol was aged and then dried in an oven at 80 °C to obtain dry gel, followed by calcination in a muffle at different temperatures (550, 600, 700, 750 and 800 °C) to obtain lithium titanate. The prepared Li_2TiO_3 was treated with 0.2 mol L^{-1} hydrochloric acid (AR, Chengdu Jinshan Chemical Reagent Co.,

Ltd., China) at 70 °C for 8 h in a water bath with a solid to liquid ratio of 5 g/500 mL. In the pickling process, the system was gently stirred at regular intervals to ensure even concentration of ions in solution, during which a few liquid samples were taken for later detection. After pickling, the mixture was filtered to obtain the sediment, followed by washing 2–3 times with distilled water. Then, the precipitate was placed on a surface plate, followed by drying in an oven at 80 °C to obtain the H_2TiO_3–lithium ion adsorbent. Finally, the adsorbent was used to adsorb Li^+ from lithium hydroxide (AR, Chengdu Kelong Chemical Reagent Co., Ltd., China) solution with a Li^+ concentration of 1.6 g L^{-1} at 25 °C and a solid to liquid ratio of 2 g/100 mL.

2.3 Characterization

The crystalline phases of the samples were investigated by an X-ray diffractometer (DX-2700, Dangdong Haoyuan Instrument Co., Ltd., China) using Cu Kα radiation at a scanning rate of 0.05° s^{-1} and a working voltage/current of 40 kV/40 mA. The viscosity of colloidal sol was measured by a digital viscometer (NDJ-5S, Shanghai Bonsi Instrument Science and Technology Co. Ltd., China). The concentration of Li^+ in solution was determined by ICP-AES (IRIS Advantage, Thermo Fisher Scientific, USA).

3 Results and discussion

3.1 Performance of the precursor sol

It was found that the prepared sol changes from opaque yellow to transparent deep yellow, and eventually becomes translucent light yellow with aging (Fig. 1). The sol system is stable after aging for 24 h, and laser permeability is the best at this time as shown in Fig. 2a. In comparison, the laser cannot pass through sol aged for 48 h as shown in Fig. 2b. However, precipitation and the layered phenomenon are not observed, which is primarily related with the zeta potential of the sol system. Colloidal sol particles are negatively charged, and they can stably exist in sol *via* mutual exclusion. Thus, the sol system is relatively stable.

3.2 Viscosity testing

The viscosities of the prepared sol system aged for different times were measured by a rotary viscometer, and then calculated according to eqn (1). Table 1 shows the variation of sol viscosity with a Ti^{4+} concentration of 0.1 mol L^{-1}.

$$\eta = k\alpha \qquad (1)$$

In eqn (1), η, k, and α are the viscosity, constant, and instrument reading, respectively.

It can be observed from Table 1 that viscosity increases from 2.13 to 10.4 mPa s upon aging from 2 to 48 h, and it further increases drastically to 324.5 mPa s upon aging from 48 to 64 h. However, the system does not transform to a gel-state. An appropriate concentration of Ti^{4+}, aging time and viscosity of the sol system are very important to ensure effective loading of
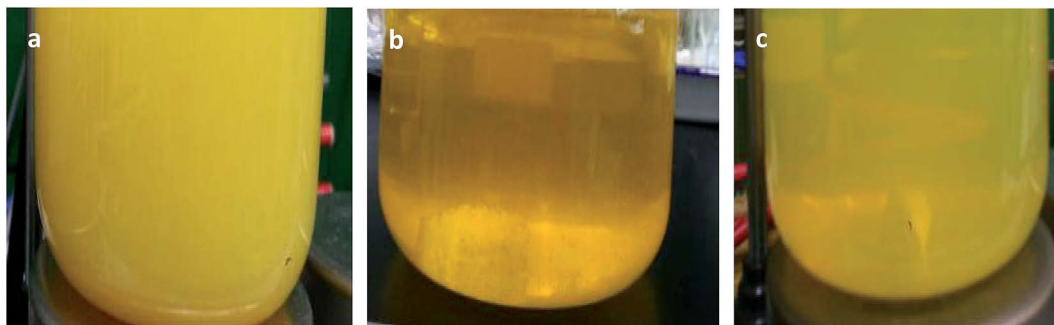
Fig. 1 Comparison of precursor sol aging (a) before aging, (b) aged for 12 h, and (c) aged for 24 h.
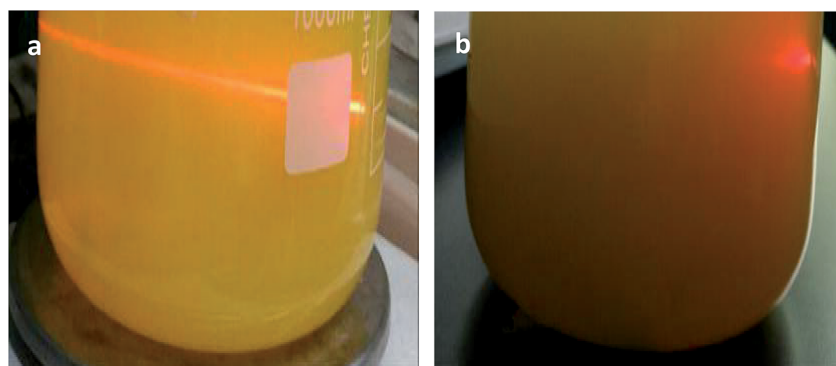

Fig. 2 Laser transmittance of precursor sol (a) aged for 24 h, and (b) aged for 48 h.

sol on ceramic foams. However, sol-systems with high viscosities are not suitable for making membranes. Therefore, a system aged for 24 h is most suited for use as a precursor sol for loading on ceramic foams because it does not form a gel-state and it also has the appropriate viscosity.

3.3 XRD analysis

As shown in Fig. 3, the diffraction peaks of the samples correspond to lithium titanate, and they are indexed to the monoclinic β-Li_2TiO_3 family (ICDD PDF #033-0831) according to the $C2/c$ (no. 15) space group. It is clear that the Li_2TiO_3 crystalline phase can be obtained after treating at 550 °C; however, the diffraction peaks are relatively low and broad. With the increase of calcination temperature, the diffraction peaks of Li_2TiO_3 become strong and sharp, implying improved crystallinity and increased grain size. When the temperature rises to 750 °C, the diffraction peaks of (002) and (−131) increase significantly. When it further increases to 850 °C, the diffraction peaks further strengthen, particularly for the crystal surfaces of (002) and (−131). It is worth mentioning that the diffraction peaks obtained in this study matches quite well with the standard card of Li_2TiO_3 (ICDD PDF #033-0831). However, in an earlier study

reported by Yao et al.,[32] the diffraction peak of the crystal surface (002), which is the strongest peak in the standard card, is quite low even after calcination at 850 °C. This is attributed to the different washing methods: centrifugal-washing in this study versus vacuum filtration-washing in their study. It is difficult to completely remove the sulfate ions via vacuum filtration-washing, and the residual sulfate ions in the filter cake have a significant effect on the crystallization orientation of
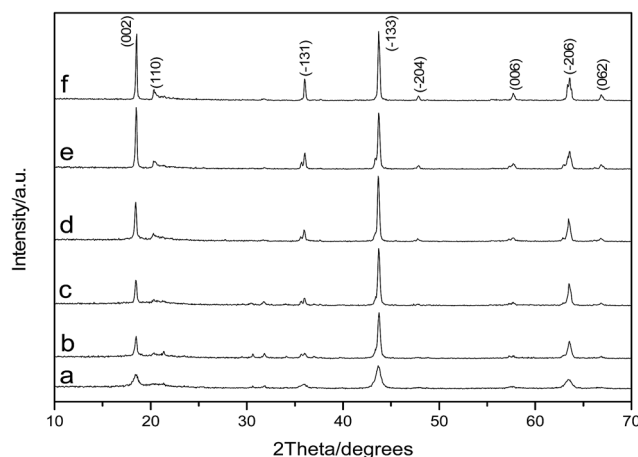

Fig. 3 XRD patterns of Li_2TiO_3 powders calcined at various temperatures (a) 550 °C, (b) 650 °C, (c) 700 °C, (d) 750 °C, (e) 800 °C, and (f) 850 °C.

Table 1 Variation of sol viscosity with aging time

Time/h	2	16	24	40	48	64
Viscosity/mPa s	2.13	2.96	3.39	5.35	10.4	324.5

lithium titanate. The titanium loss is relatively large in the pickling process when the diffraction peak intensity is not sufficiently high (550–700 °C). In contrast, an intensity that is too strong (800–850 °C) is not conducive to the subsequent lithium ion extraction. Taking into consideration the crystallization of Li_2TiO_3 and the subsequent picking process, a calcination temperature of 750 °C is the most suitable, which is in good accordance with our previous study.[33]

In addition, the XRD data of the precursor Li_2TiO_3 prepared by calcination at different temperatures were treated with MDI Jade 6 (Fig. 4); the obtained cell parameters are listed in Table 2. It can be observed from Table 2 that the cell parameters of the samples obtained at different calcination temperatures are all close to those detailed in the standard card (Li_2TiO_3, ICDD PDF #033-0381), indicating the excellent formation of Li_2TiO_3. However, there is still a slight difference between them. Taking a comprehensive consideration of a, b, c and β, the values obtained for the sample calcined at 750 °C is the closest to the standard card of Li_2TiO_3, which illustrates once again that Li_2TiO_3 precursor calcined at this temperature is optimal.

The XRD patterns of the specimens before and after acid-treatment were also investigated as shown in Fig. 5. It can be clearly observed that the diffraction peaks change markedly after pickling. The intensities of the diffraction peaks at 2θ of 43.6° and 63.5°, which are assigned to the crystal planes (−133) and (−206), respectively, apparently decrease after acid-modification. However, the diffraction peaks of (−133) and (−206) have not completely disappeared. This behavior is similar to that observed in our previous study,[26] but different from the observation in another study reported by our group.[33] This is because for a perfect structure of Li_2TiO_3, in the (−133) lattice plane, two titanium ions together with one lithium ion in the 4e Wyckoff sites are present in an ordered arrangement in the slab.[34] Once the insertion of lithium ions into the cell of

Table 2 The cell parameters of Li_2TiO_3 prepared in this work and that of Li_2TiO_3 from the standard card

Calcination temperatures	a/Å	b/Å	c/Å	β/°
550 °C	5.057	8.814	9.747	99.82
650 °C	5.122	8.774	9.765	101.07
700 °C	5.113	8.765	9.759	100.89
750 °C	5.061	8.771	9.731	99.91
800 °C	5.073	8.768	9.718	99.84
850 °C	5.058	8.772	9.724	99.89
ICDD PDF #033-0831	5.069	8.799	9.759	100.2

anatase TiO_2 takes place, the basic structure of the (−133) lattice plane is formed.[34] Formation of Li_2TiO_3 can be considered as the introduction of the specific target ion Li^+ into the lattice of TiO_2, followed by recrystallization processed by high temperature calcination to fix Li^+ in the lattice with Li^+ in the state of an ionic bond. Adsorbent preparation can be regarded as the extraction of the objective Li^+ with hydrochloric acid from the lattice, accompanied by the entrance of H^+, ensuring the electrically neutral solution. The exchange sites vacated by Li^+ due to extraction are quite narrow. However, they have special selectivity for accepting Li^+ because of the memory effect. Other ions cannot occupy the sites until both the following aspects are met: the first is a similar ionic radius; the second is an approximate energy of dehydration. Thus, the as-synthesized adsorbent has a selective adsorption performance to Li^+.[35]

As we know, Li^+ is easily combined with ionic bonds, while H^+ generally forms covalent compounds. Therefore, in the pickling process, with Li^+ extracted from the lattice, H^+ enters simultaneously, maintaining the electrical neutrality of the solution. However, hydrogen ions do not always replace lithium ions *in situ*, and the combination state of H^+ in the lithium
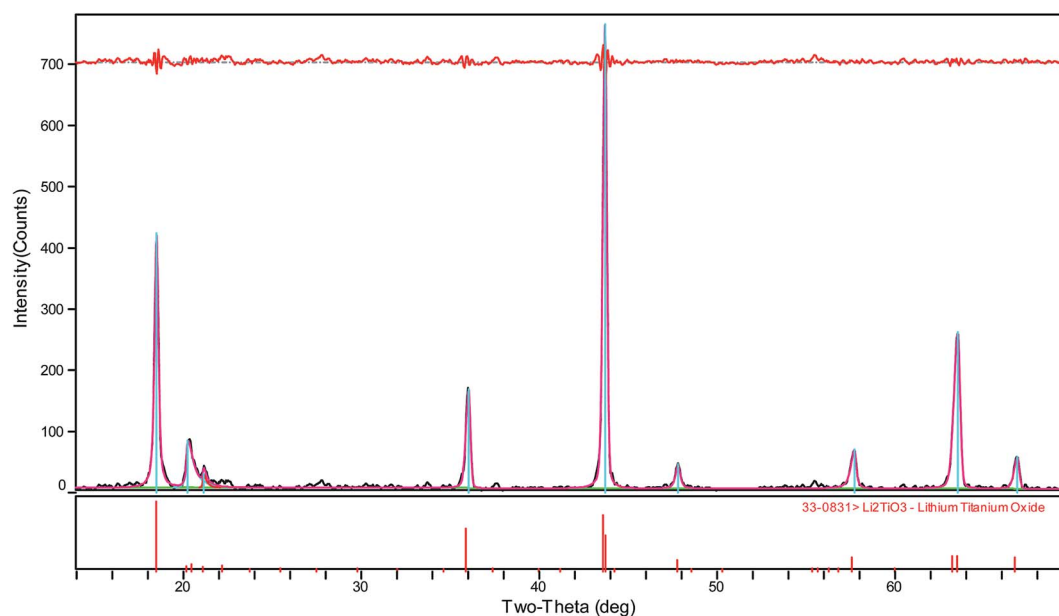

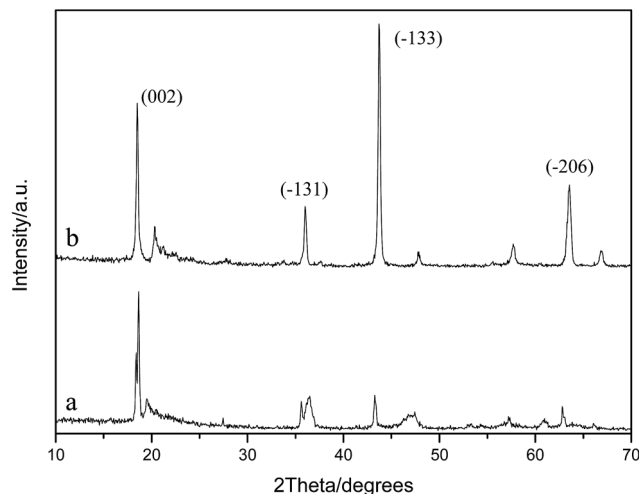**Fig. 4** Processing chart of the cell parameters of Li_2TiO_3.

Fig. 5 XRD patterns of Li_2TiO_3 before and after acid treatment (a) after pickling, and (b) before pickling.

adsorbent is different from that of Li^+ in the initial Li_2TiO_3 precursor. H^+ exists in the lithium adsorbent *via* electrostatic attraction, while Li^+ exists in the initial Li_2TiO_3 precursor through ionic bonding. As a result, the diffraction peak of (-133) decreases apparently or even disappears completely after pickling. In this study, the diffraction peak decreases sharply after pickling, indicating that a predominant proportion of Li^+ has been extracted. However, it can be observed in Fig. 5 that this diffraction peak has not completely disappeared, which is due to the following calculated lithium ion drawn-out rate of 89.50%. There are still some lithium ions that are not extracted by hydrochloric acid from Li_2TiO_3. Moreover, it can also be observed that the intensities of the diffraction peaks of (-131) and (002) slightly decrease. In addition, after acid treatment, the corresponding diffraction peaks of the (-131) and (002) crystal faces shift slightly toward high diffraction angles, indicating that the hydrogen ions exchange with lithium ions when Li_2TiO_3 is treated with hydrochloric acid, and the crystal interplanar spacing narrows after acid-treatment.[8]

3.4 Composition and adsorption performance of H_2TiO_3–lithium ion adsorbent

The composition of lithium adsorbent, H_2TiO_3, was analyzed and a suitable formula is given as $Li_xH_yTiO_3$ ($x + y = 2$, $0 \leq x < 2$, $y > 0$). The crystal structure of Li_2TiO_3 can be better described by the formula $Li[Li_{1/3}Ti_{2/3}]O_2$ in relation to its layered structure. The structure can be represented as a cubic close packing of oxygen atoms with metal atoms placed in octahedral voids.[1] Li and Ti form two types of layers in the Li_2TiO_3 structure: one (Li) layer is occupied only by Li atoms, the other $(LiTi_2)$ layer is occupied by 1/3 of Li and 2/3 of Ti.[1] Furthermore, Li^+ in the (Li) layer constitutes 75% of the total number of lithium ions in the Li_2TiO_3 structure, while the remaining 25% are located in the $(LiTi_2)$ layers.[36] The activity of Li^+ at $(LiTi_2)$ layers is different from that at (Li) layers. During the pickling process, lithium ions in the (Li) layers are first exchanged to form $H[Li_{1/3}Ti_{2/3}]O_2$,

followed by further exchange of Li^+ in the $(LiTi_2)$ layers to form the fully exchanged phase $H[H_{1/3}Ti_{2/3}]O_2$.[37] With the change in the Li^+ drawn-out ratio, the values of x and y will change, while the sum of x and y would be equal to 2. Therefore, a suitable formula to describe the composition of lithium adsorbent should be $Li_xH_yTiO_3$ ($x + y = 2$, $0 \leq x < 2$, $y > 0$).

Furthermore, the adsorption of Li^+ by the obtained lithium adsorbent was also carried out, and the result shows that the Li^+ uptake of the adsorbent (adsorption capacity) reaches 29.96 mg g^{-1} and 33.35 mg g^{-1} when the adsorption time is 1 h and 8 h, respectively. It can be observed that the lithium ion adsorbent prepared by the method described in this study also shows excellent adsorptivity. In addition, the adsorption capacity at 1 h reaches 89.8% of that at 8 h, which indicates that the adsorption of Li^+ by the adsorbent prepared by this method is quite fast. This performance is favorable for the rapid extraction of lithium from brine.

4 Conclusion

A stable peroxide lithium titanate sol was prepared by the inorganic precipitation–peptization method with titanyl sulfate as the titanium source, which is helpful for loading of Li_2TiO_3 on a suitable carrier to solve its engineering application problem derived from the separation of small solid particles from liquid, washing and regeneration. Compared with vacuum filtration-washing, centrifugal-washing assists in the formation of Li_2TiO_3, the suitable aging time of the sol is 24 h, and the appropriate calcination temperature is 750 °C. The lithium drawn-out ratio of samples runs up to 89.50% after pickling with hydrochloric acid for 8 h, and the Li^+ uptake of the adsorbent reaches 33.35 mg g^{-1}.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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