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不同酸处理钛酸锂的转型研究

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摘要: 详细研究了酸的种类和处理时间对钛酸锂转型的影响。结果显示当相同酸度的硫酸和盐酸用来对钛酸锂进行改性时,在盐酸介质中钛酸锂更容易转变为锐钛矿和金红石型二氧化钛。硫酸浓度越高,钛酸锂更容易转变为锐钛矿和金红石型二氧化钛;处理时间越长,更多的钛酸锂可以转变为锐钛矿和金红石型二氧化钛。硫酸根通过螯合双齿配位于二氧化钛,有利于稳定锐钛矿型晶相;亲电的 H^+ 和高电负性的 Cl^- 影响 Ti-O 键,导致 TiO_6 八面体中的 Ti-O 键断裂和锐钛矿型二氧化钛发生结构重排形成金红石型二氧化钛。钛锂离子筛稳定的结构和晶相组成能够保证高效、循环往复地提取锂,从这一点来看,相比于盐酸,硫酸更适合作为洗脱剂来制备钛锂离子筛,并且低浓度的硫酸是更好的选择。

关键词: 钛酸锂; 晶相转变; 螯合双齿; 结构重排

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Study on transformation of lithium titanate modified with different acids

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Abstract: The effects of kinds and concentrations of acid and treatment time on the transformation of lithium titanate (Li_2TiO_3) have been studied in detail. The results show that it is easier for Li_2TiO_3 to turn into anatase and rutile TiO_2 in hydrochloric acid medium when the same acidity of sulfuric acid and hydrochloric acid are used to treat Li_2TiO_3 for modification. The change of Li_2TiO_3 into anatase and rutile TiO_2 becomes easier for the higher the concentration of sulfuric acid. In addition, more Li_2TiO_3 can be converted to anatase and rutile TiO_2 under the longer the time of acid-treated. The sulfate radical coordinates with titanium dioxide by chelating double teeth, which is helpful for stabilizing the anatase crystalline phase. The electrophilic H^+ and the high electronegative Cl^- affect the Ti-O bond, resulting in the destruction of the Ti-O bond in TiO_6 octahedrons, and thus promoting the structural rearrangement of anatase to rutile TiO_2 . From the view point that the stable structure and crystal phase of lithium ion sieve ensuring extraction lithium ion efficiently and circularly, sulfuric acid is more suitable as eluent for the preparation of lithium ion sieve than hydrochloric acid, and sulfuric acid with a low concentration is a better choice.

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1 Introduction

Lithium is of growing importance in energy and light metal alloy fields because of its special properties. With the gradual exhaustion of land-based lithium resources, an urgent need has recently developed to extract lithium from the sea and salt lake brine, which contain an abundance of lithium resource. However, traditional precipitation, solvent extraction and salting methods^[1-2] are not suitable for extraction of lithium from sea and salt lake brine that contain low lithium concentrations. Lithium ionic sieve^[3-5], which is considered as a new approach to address the problem, has 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 as titanium lithium ionic sieve precursors are Li_2TiO_3 ^[4] and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ^[6]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is often used in lithium ion battery electrodes^[7-8]. To prepare Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, several synthetic techniques, including a solid-state reaction, a hydrolysis route, a sol-gel process and a molten-salt microwave-assisted reaction, have been reported in the literature^[3-4, 9-21]. Recently, inorganic precipitation-peptization method has also been reported^[22]. Studies have proven that it is difficult to prepare pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and rutile TiO_2 and Li_2TiO_3 are usually observed as impurity phases in the synthetic product^[23]. Hence, Li_2TiO_3 is more favorable to be used as a lithium ionic sieve precursor. Acid leaching is an effective transition process during the synthesis of lithium ionic sieve^[3-4, 24]. The concentration of eluent and immersion time have significant effects on the cyclic exchange performance of titanium lithium ion sieves, the dissolved Ti, and the composition of the product. In general, Li_2TiO_3 is modified with a low level of hydrochloric acid for a suitable time to yield lithium ionic sieves, and only the disappearance of the (-133), (-206) and (062)

planes is observed without any crystal transformation. Recently, Du *et al.*^[25] have reported that anatase and rutile TiO_2 could be obtained from the Li_2TiO_3 precursor; however, tetramethylammonium hydroxide (TMAOH) and a hydrothermal treatment are essential. Our previous work^[26] also shows that anatase and rutile TiO_2 could exist simultaneously or separately when hydrochloric acid with a moderate concentration was used to treat Li_2TiO_3 , and it also indicates that the adsorption performance of lithium ion sieve is reduced after crystal transformation. To the best of our knowledge, detailed studies regarding the specific performance of Li_2TiO_3 as a function of kinds and concentrations of acid are rare. Elucidating the process of acid leaching of lithium titanate will aid in improving the cyclic adsorption performance of lithium ion sieve (that is the purpose of this article).

2 Experiment

2.1 Preparation and treatment of Li_2TiO_3

Prior to the solid-state reaction, a mixture of TiO_2 and $\text{LiOH} \cdot \text{H}_2\text{O}$ at a molar ratio of 1/2 was mixed uniformly by wet-milling with anhydrous alcohol as the dispersant. After drying, the mixture was calcined at 750 °C for 5 h in a muffle furnace under air atmosphere, followed by cooling to room temperature in the furnace to obtain Li_2TiO_3 . Subsequently, various concentrations of sulphuric acid (0.1, 0.25, and 0.5 mol/L) and mixed acid (sulphuric acid and hydrochloric acid in molar ratios of 1 : 1, 2 : 1 and 1 : 3) were used to treat Li_2TiO_3 at 70 °C for different time. Finally, the solid product was obtained after filtration, washing, and drying.

2.2 Characterization

The crystalline phases of the samples were investigated using an X-ray diffractometer (DX-2700, Dangdong Haoyuan Instrument Co., Ltd, China) with Cu K_α radiation at a scanning rate of $0.05^\circ \cdot \text{s}^{-1}$ and a working voltage/current of

40 kV/40 mA.

3 Results and discussion

3.1 Effects of concentration of sulfuric acid and modification time

Fig. 1 is XRD patterns of Li_2TiO_3 treated with different concentrations of sulfuric acid for various time. It can be seen from Fig. 1 that the characteristic diffraction peak of anatase TiO_2 (ICDD PDF # 21-1272) at 2θ of 25.3° was detected in the product after modification with 0.1 M sulphuric acid for 150 h. The diffraction peak of $\beta\text{-Li}_2\text{TiO}_3$ (ICDD PDF # 033-0831) at 2θ of 18.7° was still high, and the intensity of the peak decreased with the prolongation of treatment time. It is indicated that when the concentration of sulphuric acid was 0.1 mol/L, the diffraction peak of metatitanate skeleton ($-\text{H}_2\text{TiO}_3$) still existed even if the modification time reached 150 h. When the sulfuric acid concentration was low, after the acid treatment, H^+ in the solution exchanged with Li^+ in Li_2TiO_3 to produce the high active $-\text{H}_2\text{TiO}_3$ which was unstable and could gradually dehydrate to form the anatase TiO_2 . However, with the prolongation of time, only transformation from $-\text{H}_2\text{TiO}_3$ to anatase TiO_2 occurred, and no rutile TiO_2 was formed. For the sample modified with 0.25 mol/L sulphuric acid, the intensity of the diffraction peak of $\beta\text{-Li}_2\text{TiO}_3$ decreased significantly after 3.5 h, but the characteristic dif-

fraction peak of anatase TiO_2 at 2θ of 25.3° was not found in the product. After 24 h, the diffraction peak of anatase TiO_2 appeared, and that of $\beta\text{-Li}_2\text{TiO}_3$ at 2θ of 18.7° completely disappeared. The peak intensity of anatase TiO_2 increased with the modification time further reached up to 72 h and 150 h. However, the characteristic diffraction peak of rutile TiO_2 (ICDD PDF # 21-1276) at 2θ of 27.5° was not observed during the whole modification process.

After modification Li_2TiO_3 with 0.5 mol/L sulfuric acid for 3.5 h, the diffraction peak of anatase TiO_2 located at 25.3° was found in the product, and the peak intensity of $\beta\text{-Li}_2\text{TiO}_3$ was quite weak. With the treatment time prolonging from 3.5 h to 150 h, the peak intensity of anatase TiO_2 increased, but the characteristic diffraction peak of rutile TiO_2 could not be detected throughout the process. The above phenomena and analysis show that, with the increase of sulphuric acid concentration, the time required for the transformation from Li_2TiO_3 into anatase TiO_2 shortens without any subsidiary conditions. In a certain concentration range, with the increase of sulphuric acid concentration, it is easier for transformation from Li_2TiO_3 into anatase TiO_2 . But, rutile TiO_2 can not be observed even if the modification time reaches 150 h when the concentration of sulphuric acid is less than or equal to 0.5 mol/L.

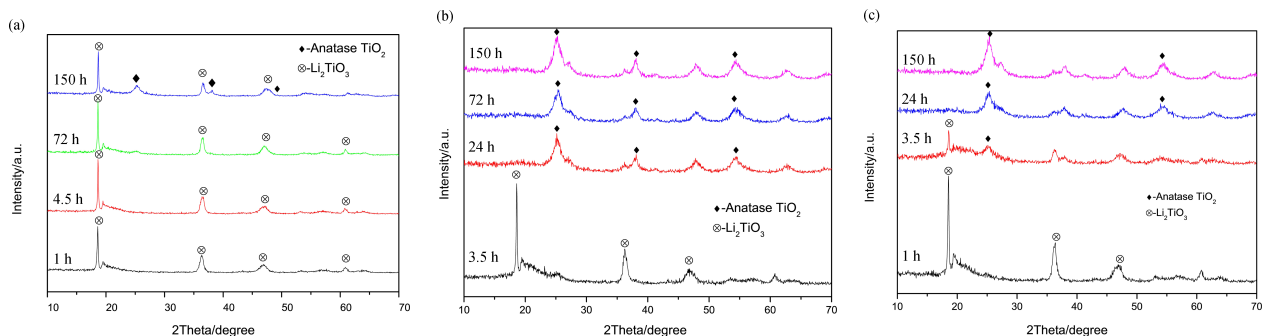


Fig. 1 XRD patterns of Li_2TiO_3 modified with various concentrations of sulphuric acid for different time (a) 0.1 mol/L, (b) 0.25 mol/L and (c) 0.5 mol/L

3.2 Effect of proportions of the mixed acid and modification time

Fig. 2 is the X-ray diffraction patterns of

Li_2TiO_3 treated with the mixed acid (1.0 mol/L H^+ , sulphuric acid and hydrochloric acid in different molar ratios) for various time. The results

show that the diffraction peaks of the samples before sulphuric acid treatment belongs to the monoclinic β - Li_2TiO_3 family (ICDD PDF # 033-0831) according to the $C2/c$ (No. 15) space group ($a = 5.0623 \text{ \AA}$, $b = 8.7876 \text{ \AA}$, $c = 9.7533 \text{ \AA}$ ^[27]). After acid-modified with MA # 1 for 1 h, obviously, diffraction peaks at 2θ of 43.6° , 63.5° and 66.9° , assigned to the crystal planes (-133) , (-206) and (062) , respectively, completely disappeared. The intensity of the diffraction peak of (002) and (-131) crystal surface decreased obviously, and these two peaks shifted to the higher diffraction angles after acid-modification.

The above-mentioned indicates that hydrogen ions exchange with lithium atoms when Li_2TiO_3 is treated with the mixed acid. The crystal interplanar spacing of the samples narrows after acid-treatment^[4]. This result is similar to our previous work^[26] in which Li_2TiO_3 was treated with 0.4 mol/L hydrochloric acid for 1 h. Anatase TiO_2 appeared in the sample when the treatment time was extended from 1 h to 4.5 h, and the diffraction peaks of crystal surface (002) and (-131) disappeared completely. The diffraction peaks of the samples were quite similar as the modification time prolonged from 4.5 h to 24 h, which was different from the result in our previous work^[26],

in which the diffraction peak of the sample was quite similar in locations and diffraction angles when the modification time was extended from 1 h to 12 h. However, the diffraction peak was obviously weakened when the time increased to 24 h, and the positions of the diffraction peaks were quite different from that of 12 h. In this work, the crystal phase of the samples changed significantly when the modification time further increased up to 150 h. The characteristic diffraction peak of rutile TiO_2 was observed in the specimens, indicating the formation of rutile TiO_2 . In addition, the intensity of the characteristic diffraction peak of anatase TiO_2 increased gradually from 4.5 h to 150 h. In our previous work^[26], the characteristic diffraction peak of rutile TiO_2 could be detected in the samples after a treatment with 1.0 mol/L hydrochloric acid for only 5.5 h. It can be concluded that, in a solution with an enough acidity, Li_2TiO_3 can easily transform into an anatase TiO_2 phase and can even change into a rutile TiO_2 phase. With the same acidity of hydrochloric acid and sulfuric acid for the treatment, Li_2TiO_3 is more easily transformed into anatase TiO_2 and rutile TiO_2 phase in a hydrochloric acid medium.

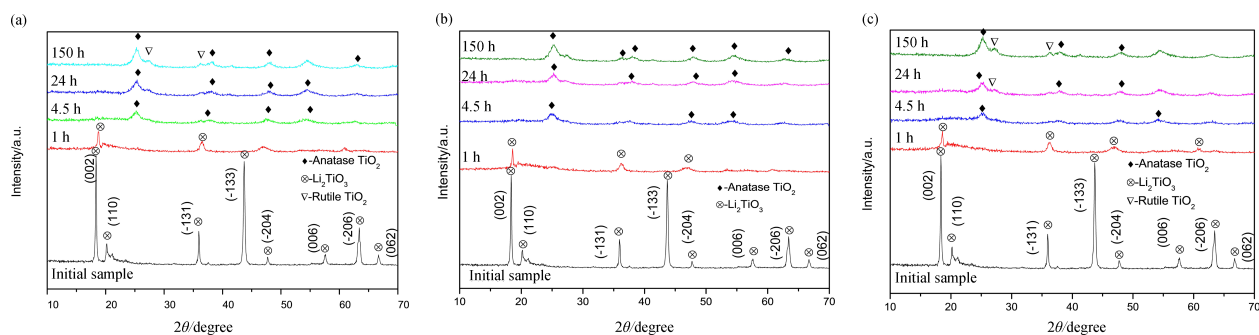


Fig. 2 XRD patterns of Li_2TiO_3 modified with the mixed acid (1.0 mol/L H^+ , sulphuric acid and hydrochloric acid in different molar ratios) for various time (a) 1 : 1, labeled as MA # 1; (b) 2 : 1, labeled as MA # 2; and (c) 1 : 3, labeled as MA # 3

For MA # 2, the result was similar to that of Li_2TiO_3 treated with MA # 1 for 1 h and 4.5 h. The intensity of the characteristic diffraction peak of anatase TiO_2 at 2θ of 25.3° for MA # 1 was higher than that of MA # 2 when treating 24 h.

As the modification time increased to 150 h using MA # 2, only diffraction peak of anatase TiO_2 was found in the products, and no diffraction peak ascribed to rutile TiO_2 appeared. 24 h was needed for the initial appearance of characteristic

diffraction peak of rutile TiO_2 at 2θ of 27.5° when MA # 3 was used to treat Li_2TiO_3 for modification. Besides, the intensity of diffraction peak of rutile TiO_2 was higher than that using MA # 1 when the modified time increased up to 150 h.

The above results show that rutile TiO_2 were both found in the products when MA # 3 and MA # 1 were used to treat Li_2TiO_3 for 150 h, and the intensity of the former was higher than that of the latter. However, no rutile TiO_2 but only anatase TiO_2 appeared when MA # 2 was employed to modify Li_2TiO_3 for the same amount of time. In a previous work of Yang^[28], it was suggested that in the process of iron doped TiO_2 , the sulfate radical coordinates with titanium dioxide by chelating double teeth, which is beneficial to stabilizing the anatase crystalline phase and oxygen vacancy, and increasing the solid acidity. Therefore, it can be concluded that, under a certain concentration of H^+ , the modification of Li_2TiO_3 with hydrochloric acid is beneficial to the transformation of products into rutile TiO_2 as compared with that with sulfuric acid.

3.3 Effect of mixed acid and sulphuric acid treatment on Li_2TiO_3

Fig. 3 is X-ray diffraction pattern after treating Li_2TiO_3 for 150 h with sulfuric acid (1.0 mol/L H^+) and MA # 1. After the treatment with sulfuric acid for 150 h, only anatase TiO_2 appeared, while rutile TiO_2 was observed after modification with MA # 1 for 150 h. In addition, combining with previous discussions, it can be concluded that when the H^+ ions concentration is the same, the greater proportion of hydrochloric acid in the mixed acid, the more rutile TiO_2 will appear. This phenomenon may be related to sulfate ion^[28], and may also be related to chloride ion. In our previous work^[26], it was suggested that anatase and rutile TiO_2 could exist simultaneously when the hydrochloric acid concentration was moderate. Many H^+ ions were residual in the solution apart from H^+ exchanged with Li^+ . These electrophilic protons could easily attack the Ti-O bond in the structure of the TiO_6 octahed-

ron. As a result, the electron cloud shifts away from Ti, thereby imparting a strong electrophilic character to the Ti atom. Simultaneously, the electrophilic Ti atom attracted Cl^- in the solution, leading to the destruction of the Ti-O-Ti bond in the TiO_6 octahedron and to structural rearrangement. Thus, a more stable rutile phase was produced^[29].

When sulfuric acid with the same concentration of H^+ was used as medium to treat Li_2TiO_3 , the sulfate radical coordinated with titanium dioxide by chelating double teeth, which was beneficial to stabilizing the anatase crystalline phase and oxygen vacancy, and increasing the solid acidity. Therefore, the concentration of H^+ in the solution decreased, which was not conducive to the transformation from anatase TiO_2 to rutile TiO_2 . Besides, the lack of highly electronegative Cl^- in the solution also contributed to the difficult destruction of the Ti-O-Ti bond in the TiO_6 octahedron and the difficult structural rearrangement. It can be concluded that sulfate radical is beneficial to stabilizing the anatase crystalline phase, and thus it is not easy for transformation from anatase TiO_2 to rutile TiO_2 in the process of crystal transformation of H_2TiO_3 -lithium titanate via acid modification.

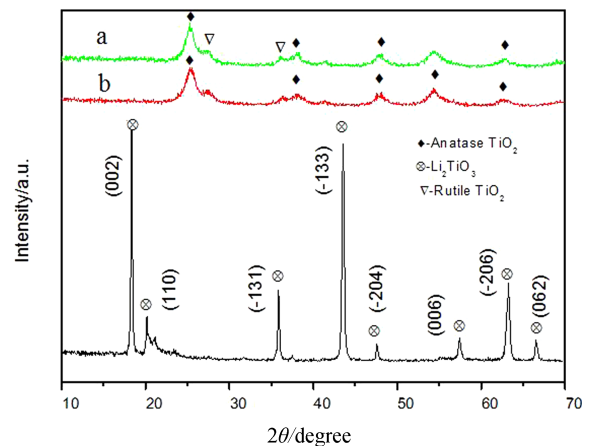


Fig. 3 XRD patterns of Li_2TiO_3 treated with (a) MA # 1 and (b) sulphuric acid (1.0 mol/L H^+) for 150 h

4 Conclusions

It is easier for Li_2TiO_3 to turn into anatase

and rutile TiO_2 in hydrochloric acid medium when sulfuric acid and hydrochloric acid with the same concentration of H^+ are used to treat Li_2TiO_3 . The higher the concentration of sulfuric acid, the easier the change of Li_2TiO_3 into anatase and rutile TiO_2 , and the longer the treatment time, the more the transformation of Li_2TiO_3 into anatase and rutile TiO_2 . Sulfate radical is beneficial to stabilizing the anatase crystalline phase. The electrophilic H^+ and highly electronegative Cl^- promote the structural rearrangement of anatase to rutile TiO_2 . The application of lithium ion sieve is to extract lithium ion efficiently and circularly, and thus the stability of structure and crystal phase must be good. So, sulfuric acid is more suitable to be used as the eluent to prepare lithium ion sieve than hydrochloric acid, and sulfuric acid with a low concentration is a better choice.

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