Synthesis of $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$ and its Selectivity to Li^+ Exchange

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The ion-exchanger $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$ of spinel type was prepared by means of the solid state reaction crystallization method. Its ion-exchange properties for alkali ions such as saturation capacity of exchange and distribution coefficient were determined. $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$ was characterized by X-ray diffraction method. The acid treatment of $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$ causes Li^+ extraction ratio to change from 50 to 90 %, while dissolution of Ti^{4+} is less than 7.5 %. This inorganic ion-exchanger ($\text{Li}_2\text{Ti}_{1.5}\text{O}_4$) has the saturation capacity of exchange for Li^+ higher than those for other alkali ions, the saturation capacity of exchange for Li^+ reaches to 7.4 mmol/g, LiTiO-775(H) has a higher selectivity of ion exchange for Li^+ than for other alkali ions. These results show that LiTiO-775(H) has better memory and selectivity of ion exchange and higher capacity of ion exchange for Li^+ . It is a kind of prospective ionic sieve for Li^+ .

Key Words: Complex oxide, Lithium, Ion exchange, $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$.

INTRODUCTION

The ocean is called the "treasure house of resources". The ocean is dissolved with the inexhaustible chemical substances and energy. The world has endowed wide attention to the development of marine and utilization of marine resources. There are about 230 billion tons of lithium reserves in the sea water, far more than the reserves on the land. Lithium and its compounds are widely used in ceramics, medicine, air conditioning, catalysts, high-energy lithium battery and light aluminum alloy, etc., especially for the thermonuclear reaction, lithium is the essential raw material^{1,2}. The researches of adsorption to take the lithium directly from seawater has undergone over 20 years^{3,4}. In this paper, the synthesis, structure and ion exchange of the Li-Ti composite oxide inorganic ion exchanger of $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$ are discussed. The experimental results have been proved that the inorganic material has good selectivity and higher capacity of exchange for Li^+ in solution.

EXPERIMENTAL

Li_2CO_3 and TiO_2 were all analytical reagents; pure ethanol; D/max-A type X-ray diffraction instrument; Dx-170 type ion chromatogram instrument; XQM planetary ball mill; AA-670 atom absorption spectrum instrument; tubular-furnace.

Synthesis and identifiable of $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$: The pure ethanol was dropped into a XQM planetary ball mill mixed powder of Li_2CO_3 and TiO_2 with a Li/Ti mole ration of 2:1.5 at the condition of constant rate churning. After 8 h, the mixture was mixed

completely. After mixing fully, the mixture was pressed to tablet by tablet press machine. Then the tablet was heat-treated for 4.5 h at 775 °C to obtain the Li-Ti oxide, the sample was designed as LiTiO-775 , whose theoretical formula is $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$. Then it was analyzed of X-ray diffraction and compared to literature^{3,4}.

Composition analysis: A 0.2 g portion of sample was dissolved with acid. The Li and Ti contents were determined by atomic absorption spectrometry.

Cation extraction of LiTi oxide and acid modification: Four 0.200 g portions of sample (LiTiO-775 oxides) were immersed in a HNO_3 solution (50 mL) of 0.01, 0.1, 1 and 10 M, respectively with shaking in constant temperature water at 25 °C. After 3 days, take the supernatant solution to determine the cation concentration, test its acid proof ability and the extraction ratio of Li^+ , Ti^{4+} .

A 5 g portion of sample (LiTiO-775) was immersed in a 1 M HNO_3 solution (500 mL) with intermittent shaking in constant temperature water at 25 °C. After 7 days, remove the supernatant solution and add new HNO_3 solution. Repeating that for twice, then the initial sample was transformed to H-type sample, washed with water and air-dried. The sample obtained by thermal crystallized at 775 °C and acid modified was designated as LiTiO-775 (H) . The composition was determined by the method referred in 1.2 and the H content was calculated by subtraction method.

Saturation capacity of exchange: Weighed five 0.5 g portions of LiTiO-775 (H) , then each portion was immersed

in a 0.1 M solution (10 mL), containing Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ , respectively, diluted to 100 mL, shaken in constant temperature water at 25 °C. After saturation exchanging (namely, after 10 days by literature^{3,4} the solutions were filtered by subminiature aperture sieve and the cation concentration was determined. Last, the inorganic exchanger saturation capacity of exchange for alkali-metal-ions obtained by decrease quantity.

Distribution coefficient (K_d): After weighing four 0.100 g portions of LiTiO-775 (H), each portion of sample was immersed in a 0.05 M mixed solution (0.200 mL) containing Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ (Cl^-/OH^- ratios are different in each solution, $\text{C}(\text{Cl}^-) + \text{C}(\text{OH}^-) = 0.1 \text{ M}$, $\text{C} = \text{Li}^+$, Na^+ , K^+ , Rb^+ and Cs^+). The alkali-metals ions total concentration all was $1.0 \times 10^{-3} \text{ M}$ by adding 9 mL distilled water. After the samples were shaken for 7 days in constant temperature water at 25 °C and were filtered, cation concentrations in each sample were obtained.

RESULTS AND DISCUSSION

Compound and appraisement of $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$: The X-ray diffraction pattern of compound metal oxide ($\text{Li}_2\text{Ti}_{1.5}\text{O}_4$), crystallized was shown in Fig. 1. The structure of compound metal oxide $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$ crystallized at 775 °C was much perfect.

Fig. 1. Powder's X-ray figures of $\text{Li}_{1.97}\text{Ti}_{1.47}\text{O}_{3.95}$ crystal

From chemical analysis, the composition of LiTiO-775 is $\text{Li}_{1.97}\text{Ti}_{1.47}\text{O}_{3.95}$ was established, whose chemical component is basically corresponded with the composition of spinel-type metal oxides.

Cation extraction of compound oxide LiTiO and acid modification: The extraction ration of Li^+ and Ti^{4+} from LiTiO-775 in different concentration HNO_3 solution is shown in Fig. 2. Fig. 2 showed the extractabilities of Li^+ are 50 to 90 % and Ti^{4+} are 2.8-7.5 %. Those indicate that the extractabilities of Li^+ are higher than Ti^{4+} when exchanger was immersed in 1 M acid solution, corresponding with the exchanger condition was better (1 N, Li^+ 83 %, Ti^{4+} 5.2 %).

The analysis indicate the composition of LiTiO-775(H) was $\text{H}_{1.64}\text{Li}_{0.33}\text{Ti}_{1.39}\text{O}_{3.75}$, whose component of 82 % Li^+ transformed to H^+ compared with the composition $\text{Li}_{1.97}\text{Ti}_{1.47}\text{O}_{3.95}$ before acid-treated. Then the specific Li^+ of exchanger were extracted fulfill basically and remained the H-type identified with initial type.

Fig. 2. Extraction ratio of cations from LiTiO-775 in nitric acid solution

Saturation capacity of exchange: The relation between radius and saturated ion exchange capacity of LiTiO-775(H) for alkali was shown in Fig. 3. Fig. 3 suggested that the capacity of exchange for Li^+ was much higher than those for other alkali ions. The capacity for Li^+ is 7.4 mmol g^{-1} . It proved that the ion exchange synthesized has higher capacity of exchange and better remembering of exchange for Li^+ . The effect factors of saturation capacity of exchange of LiTiO-775 (H) are: The Li^+ in exchange solution must be removed previously, because Li^+ exchange with exchanger vacancy site when existing too much Li^+ . The experimental results shown that the exchange capacity of ion exchanger for Li^+ is much higher than those for other alkali ions in thin solution, which indicate that the ion-exchange reaction is carried out between and bare ions. At the time of exchange, a Li^+ was replaced by one H^+ . Li^+ not only entered the vacancy site but also exchanged with the H^+ of surface. Therefore, LiTiO-775 (H) has a higher exchange capacity for Li^+ .

Fig. 3. Relation between ion radius and saturated ion exchange capacity of LiTiO-775 (H) for alkali ions

Distribution coefficient (K_d): K_d values can be the token of exchange selectivity of LiTiO-775 (H) for correlate ions. Shown in Fig. 4, K_d values of LiTiO-775 (H) for alkali ions are larger and larger with an increase pH over the pH region studied. The selectivity sequence of LiTiO-775(H) for alkali metal ions as follows:

It indicates that LiTiO-775 (H) has a better ion selectivity for Li^+ . Ion-exchange reaction is reversible reaction. The

Fig. 4. Distribution coefficient of LiTiO-775(H) for alkali ions

reaction of H^+ in ion-exchanger with alkali metal ions in solution as follows (example for Li^+):

Conclusion

The results indicate that the $\text{Li}_2\text{Ti}_{1.5}\text{O}_4$ of spinel-type metal oxide show a capacity extraction/insertion of Li^+ in the aqueous phase, mainly by an ion-exchange mechanism. The Li^+ -extracted samples show a high selectivity and a large capacity for Li^+ among alkali metal ions.

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