



Li⁺ Extraction/Insertion Reaction with Li_{1.5}Ti_{1.625}O₄ Spinel in the Aqueous Phase

JINHE JIANG

Department of Chemistry and Chemical Engineering, MicroScale Science Institute, Weifang University, Weifang 261061, P.R. China

Corresponding author: Fax: +86 536 8785802; Tel: +86 536 8785802; E-mail: jiangjinhe2006@163.com

(Received: 25 October 2011;

Accepted: 20 August 2012)

AJC-11989

Spinel-type metal oxides, lithium-titanium oxide (Li_{1.5}Ti_{1.625}O₄), was prepared by a solid state reaction crystallization method. The extraction/insertion reaction with this material was investigated by X-ray, saturation capacity of exchange and K_d measurement. The experimental results have proved that the acid-treated sample has a capacity of exchange 6.1 mmol g⁻¹ for Li⁺ in the solution, the chemical analysis showed that the Li⁺ extraction/insertion progressed mainly by ion-exchange mechanism and surface adsorption.

Key Words: Extraction/insertion reaction, Spinel-type metal oxides, Ion-exchange mechanism, Li_{1.5}Ti_{1.625}O₄.

INTRODUCTION

The inorganic ion-exchange preparation has the advantage of thermo-stability and radiation resistance, simple synthesis and good selectivity, *etc.* Apart from that, it appears the fine substance in dealing with nuclear waste, gathering and separating of metal ions and chromatogram analysis^{1,2}.

With the study of ion-sieve-type inorganic materials progressed, the inorganic ion-exchange materials having special "sieve sites" structure can be obtained by inserting specific ions in inorganic compound and fixing the ions inserted by particular approach. Then extract the specific ions in the premise of maintaining the initial crystallization structure. In this paper, the solid state reaction crystallization method was used to synthesize the Li_{1.5}Ti_{1.625}O₄ of spinel-type oxide, whose composition and structure are different from those in literature^{3,4}, the experimental results have proved that the inorganic material has good selectivity and higher capacity of exchange for Li⁺ in the solution removed Li⁺ previously. Moreover, the cost is low and its application prospect is significant.

EXPERIMENTAL

Li₂CO₃ and TiO₂ 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 characterization of Li_{1.5}Ti_{1.625}O₄: The pure ethanol was dropped into a XQM planetary ball mill mixed powder of Li₂CO₃ and TiO₂ with a Li/Ti mole ration of 1.5:1.625 at the condition of constant rate churning. After 8 h, the mixture was mixed completely. After proper mixing, the

mixture was pressed to tablet by tablet press machine. Then the tablet was heat-treated for 4.5 h at 750 °C to obtain the Li-Ti oxide, the sample was designed as LiTiO-750, whose theoretical formula is Li_{1.5}Ti_{1.625}O₄. Then it was analyzed by 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-750 oxides) were immersed in a HNO₃ solution (50 mL) of 0.01, 0.1, 1.0 and 10.0 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 ration of Li⁺, Ti⁴⁺.

A 5 g portion of sample (LiTiO-750) was immersed in a 1 M HNO₃ solution (500 mL) with intermittent shaking in constant temperature water at 25 °C. After 7 days, remove the supernatant solution and add new HNO₃ 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 750 °C and acid modified was designated as LiTiO-750 (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: Weigh five 0.5 g portions of LiTiO-750 (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^{3,4} (namely, after 10 days) 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-750 (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, C(Cl⁻) + C(OH⁻) = 0.1 M, C = Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺). The alkali-metal ions total concentration all was 1.0×10^{-3} 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 samples were obtained.

RESULTS AND DISCUSSION

Compound and appraisalment of Li_{1.5}Ti_{1.625}O₄: The X-ray diffraction pattern of compound metal oxide (Li_{1.5}Ti_{1.625}O₄), crystallized was shown in Fig. 1. The structure of compound metal oxide Li_{1.5}Ti_{1.625}O₄ crystallized at 750 °C was much perfect.

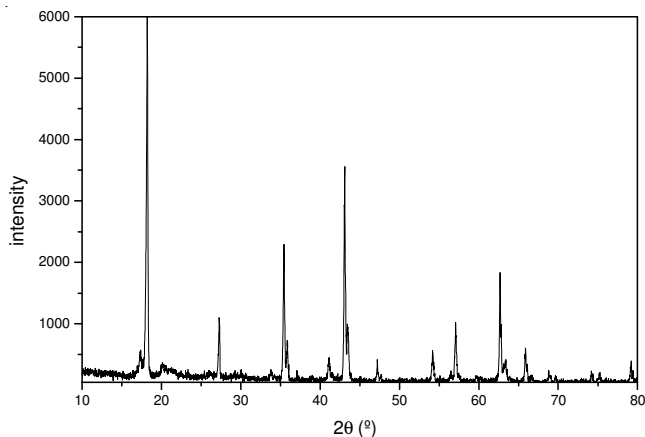


Fig. 1. Powder's X-ray figures of Li_{1.48}Ti_{1.61}O_{3.96} crystal

From the chemical analysis, the composition of LiTiO-750 is Li_{1.48}Ti_{1.61}O_{3.96}, 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 ratio of Li⁺ and Ti⁴⁺ from LiTiO-750 in different concentration HNO₃ solution is shown in Fig. 2. Fig. 2 shows the extractabilities of Li⁺ are 52-89 % and Ti⁴⁺ are 2.9-7.9 %. Those indicate that the extractabilities of Li⁺ are higher than Ti⁴⁺ when exchanger was immersed in 1 M acid solution, corresponding with the exchanger condition was better (1 N, Li⁺ 82 %, Ti⁴⁺ 5.8 %).

The analysis indicate the composition of LiTiO-750(H) was H_{1.21}Li_{0.27}Ti_{1.52}O_{3.96}, whose component of 82 % Li⁺ transformed to H⁺ compared with the composition Li_{1.48}Ti_{1.61}O_{3.9} before acid-treated. Then the specific Li⁺ of exchanger were extracted fulfill basically and remained the H-type identified with initial type.

Saturation capacity of exchange: The relation between radius and saturated ion exchange capacity of LiTiO-750 (H) for alkali was shown in Fig. 3. Fig. 3 suggested that the

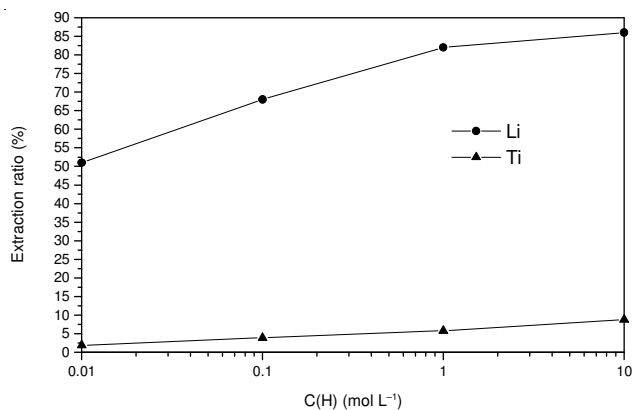


Fig. 2. Extraction ration of cations from LiTiO-750 in nitric acid solution

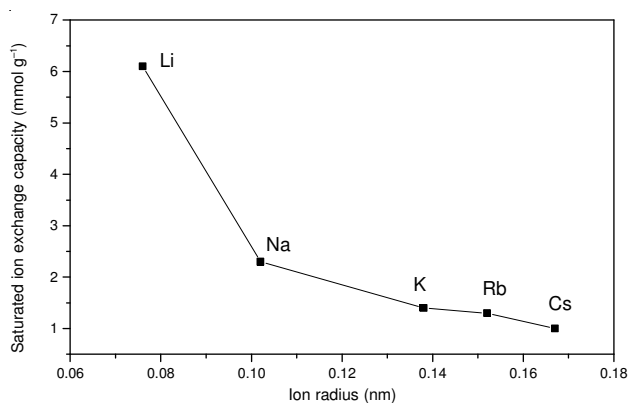


Fig. 3. Relation between ion radius and saturated ion exchange capacity of LiTiO-750 (H) for alkali ions

capacity of exchange for Li⁺ was much higher than those for other alkali ions. The capacity for Li⁺ is 6.1 mmol g⁻¹. It proves 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-750 (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 suggest that the exchange capacity of ion exchanger for Li⁺ is much higher than those for other alkali ions in diluted 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 exchange with the H⁺ of surface. Therefore, LiTiO-750 (H) has a higher exchange capacity for Li⁺.

Distribution coefficient (K_d): K_d values can be the token of exchange selectivity of LiTiO-750 (H) for correlate ions. Fig. 4 showed the K_d values of LiTiO-750 (H) for alkali ions are larger and larger with an increase pH over the pH region studied. The selectivity sequence of LiTiO-750(H) for alkali metal ions as follows:



It indicates that LiTiO-750 (H) has a better ion selectivity for Li⁺. Ion-exchange reaction is reversible reaction. The reaction of H⁺ in ion-exchanger with alkali metal ions in solution as follows (example for Li⁺):



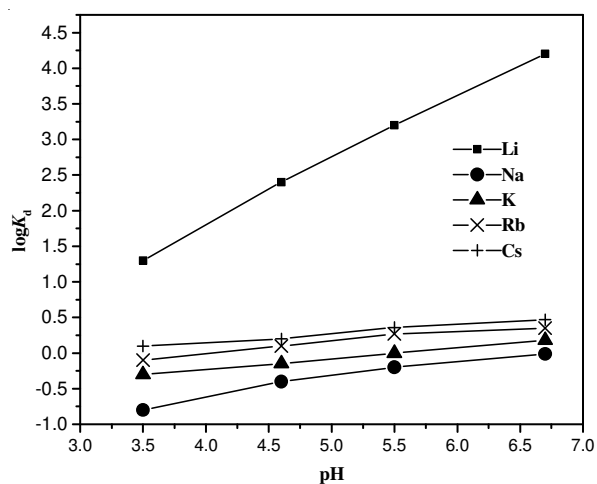


Fig. 4. Distribution coefficient of LiTiO-750(H) for alkali ions

Conclusion

The results indicate that the $\text{Li}_{1.5}\text{Ti}_{1.625}\text{O}_4$ 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.

REFERENCES

1. J.H. Jang, D.Q. Dong, G.H. Cheng, J.Q. Liu and J. Li, *J. Rare Metal*, **26**, 121 (2007).
2. S.C. Zhang and G.F. Zhou, *J. Ion Exchange Adsorption*, **14**, 351 (1998).
3. Y.F. Liu, Q. Feng and K. Ooi, *J. Colloid Interf. Sci.*, **163**, 130 (1994).
4. D.Q. Dong, F.B. Zhang, G.L. Zhang and Y.F. Liu, *J. Chin. J. Inorg. Chem.*, **9**, 20 (2004).