

STUDY OF THE INSERTION AND EXTRACTION MECHANISM OF $\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$

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Abstract: The metal oxide $[\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3]$ was synthesized by solid state reaction crystallization method in certain temperature. It was an inverse spinel type compound metal oxide. The extraction/insertion reaction of this material was studied by X-ray, saturation exchange capacity value and distribution coefficient (K_d) measurement value. In terms of its composition and chemical metrology, this inverse spinel material is very comprehensive; it is worth noting that it can be inserted or extracted by other substitutional ions and changes in lithium and oxygen stoichiometry while maintaining their crystal structure. The metal oxide $[\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3]$ is inorganic Li^+ exchanger which has an ion-memory capacity. It has high exchange selectivity ability for Li^+ . This metal oxide can be used to separate or extract Li^+ in aqueous solution. The experimental result has confirmed inverse spinel type compound metal oxide which was treated by acid could attain $9.7 \text{ mmol} \cdot \text{g}^{-1}$ Li^+ exchanged capacity.

Keywords: *insertion and extraction rate, ion-exchange mechanism, inverse spinel type, metal oxide $\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$, selective capability*

INTRODUCTION

Inorganic ion-exchange preparation shows the good characteristics in tackling nuclear waste, collection and separation of metal ions and chromatographic analysis. It is significant to look for the Li^+ exchange preparation which has the specific selectivity and memory. The emergence of ion memory inorganic material (ion sieve) makes it possible to extract directly lithium from salt water [1, 2]. In this paper, the inorganic ion-exchange preparation ($\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$) which has an inverse spinel structure was synthesized by solid state reaction crystallization method. This was different from the report in literatures [3, 4]; besides, its ion-exchange characteristics were also studied. The $\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$ was synthesized by solid state reaction thermal crystallization from lithium carbonate (Li_2CO_3), titanium dioxide (TiO_2) and manganese dioxide (MnO_2) at $700 \sim 1000\text{ }^\circ\text{C}$ [5 – 8].

EXPERIMENTAL SECTION

Reagent and instruments

Li_2CO_3 , MnO_2 and TiO_2 were all analytical reagents; pure ethanol; D/max-A type X-ray diffraction instrument (Rigaku International, Japan); Dx-170 type ion chromatogram instrument (Shimadzu, Japan); XQM planetary ball mill (Beijing Uesiphy Development Company Limited, China); AA-670 atom absorption spectrum instrument (Thermo Fisher Scientific, USA); SX2 type box type resistance furnace (Longkou Electric Furnace Factory, China).

Synthesis and identification of $\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$

The pure ethanol was poured into XQM planetary ball mill which has a Li:Mn:Ti mole ratio of 3:0.5:0.25 from the Li_2CO_3 , MnO_2 and TiO_2 powder that already existed in planetary ball mill and the planetary ball mill was churned at constant rate. 8 hours later, the compound would be mixed wholly. After mixing completely, it was pressed into tablet by tablet press machine. This sample was heated at $800\text{ }^\circ\text{C}$ for 4.5 h to get the Li-Mn-Ti metal compound. This sample was regarded as LiMnTi-800 and its theoretic chemical structure was $\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$. Then it was analyzed by X-ray diffraction and was compared with other literatures [3, 4].

Composition analysis: 0.2 g sample component was dissolved by HNO_3 and the components of Li^+ , Mn^{4+} and Ti^{4+} were determined by atomic absorption spectrometry.

The cations extraction of metal compound Li-Mn-Ti and acid modification

Four samples (0.2 g each) of (LiMnTi-800) were poured into HNO_3 solution (50 mL) which respectively has 0.01, 0.1, 1 and 10 M concentration. Then the four sample components were shaken at $25\text{ }^\circ\text{C}$ constant temperature water. After 3 days, the supernatant solution was separated from the four sample solution to detect their cation concentration, acid proof ability and the extraction ration of Li^+ , Mn^{4+} , Ti^{4+} .

5.0 g sample component (LiMnTi-800) was poured into 1 M HNO_3 solution (500 mL) and was shaken intermittently at 25 °C constant temperature water. 7 days later, the supernatant solution was taken away and was added new HNO_3 solution. Repeat this process for twice, and the initial sample was transformed to H-type sample. Then it was washed with water and air-dried. This sample was thermal crystallized at 900 °C and acid modified and is designated as LiMnTi-800(H).

Saturation exchange capacity

Five samples of LiMnTi-800(H) (0.5 g each) were respectively poured into 0.1 M solution (10 mL) which has already existed the ion of Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ , then the solution was diluted to 100 mL and was shaken at 25 °C constant temperature water. After that, those cations were moved and were exchanged by other metal ions [9, 10]. Behind the saturation exchanging, (in other words, after 10 days by literatures [3, 4]) the solutions were filtered by subminiature aperture sieve and the cation concentrations could be determined too. Meanwhile, make a blank experiment. Finally, through the method of decreasing quantity, we could obtain the exchanged capacity of this inorganic exchanger saturation for alkali-metal-ions.

Distribution coefficient (K_d)

Four samples of LiMnTi-800(H) (0.1 g each) were respectively poured into 0.05 M mixed solution (0.200 mL) which has already existed the ion of Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ (There were different Cl^-/OH^- ratios 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 total concentration of alkali-metals ions attained 1.0×10^{-3} M when 9 mL distilled water was added. After that, these samples were continuously shaken 7 days at 25 °C constant temperature water and were filtered. Finally, the cation concentration of each sample solution would rich the saturation and the cation concentration would be determined.

RESULTS AND DISCUSSIONS

Compound and appraisalment of $\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$

The X-ray diffraction diagram of compound metal oxide component ($\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$) which was crystallized is shown in Figure 1 (the crystal framework of the compound is perfect at 800 °C)

Through chemical analysis, the LiMnTi-800 chemical structure is $\text{Li}_{2.96}\text{Mn}_{0.48}\text{Ti}_{0.24}\text{O}_{2.98}$, and its chemical constituent is generally consistent with the inverse spinel type compound metal oxide.

The cations extraction of metal compound Li-Mn-Ti and acid modification

The extractive ration of Li^+ , Mn^{4+} and Ti^{4+} from LiMnTi-800 existed in different concentration HNO_3 solution is shown in Figure 2. The Li^+ extractive capabilities are 45 - 85 %, Mn^{4+} are 6.8 - 15.7 %, and Ti^{4+} are 2.6 - 8.4 %. These data suggest that Li^+

extractive capability is higher than Mn^{4+} and Ti^{4+} when the exchanger was poured into 1 M acid solution. Phosphoric acid [11] and nitric acid [12] have similar behaviors to hydrochloric acid. That is: this exchanger condition is better ($1 \text{ mol}\cdot\text{L}^{-1} \text{HNO}_3$, Li^+ 79 %, Mn^{4+} 10.3 %, Ti^{4+} 6.4 %).

The X-ray diffraction of LiMnTi-800(H) modified by HNO_3 is illustrated in Figure 1. From the diagram, the LiMnTi-800(H) structure is basically steady. It is the inverse spinel oxide type structure too. It shows that the exchanger is stable. Through analysis and discussion, the LiMnTi-800(H) structure is proved to be the $\text{H}_{2.34}\text{Li}_{0.62}\text{Mn}_{0.43}\text{Ti}_{0.22}\text{O}_{2.78}$. In its chemical constituent, 79 % Li^+ is transformed to H^+ compared with the $\text{Li}_{2.96}\text{Mn}_{0.48}\text{Ti}_{0.24}\text{O}_{2.98}$ constituent before acid treatment. Subsequently, the Li^+ in exchanger is extracted basically completely and it still remains the H-type structure which is identical with the initial type.

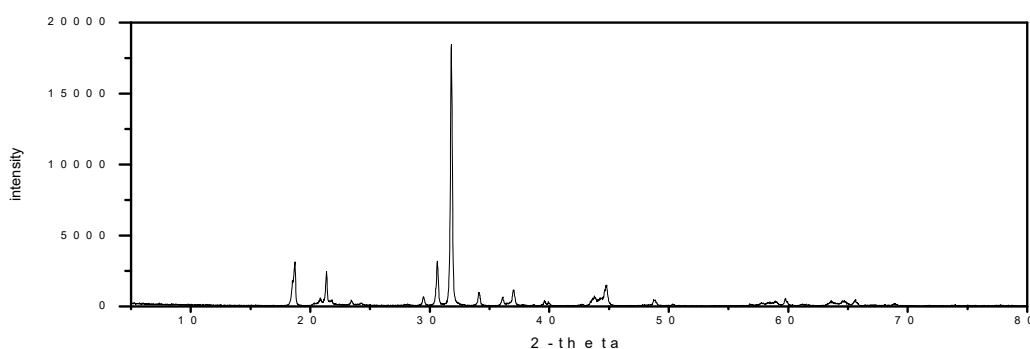


Figure 1. The powder's X-ray figures of $\text{Li}_{2.96}\text{Mn}_{0.48}\text{Ti}_{0.24}\text{O}_{2.98}$ crystal

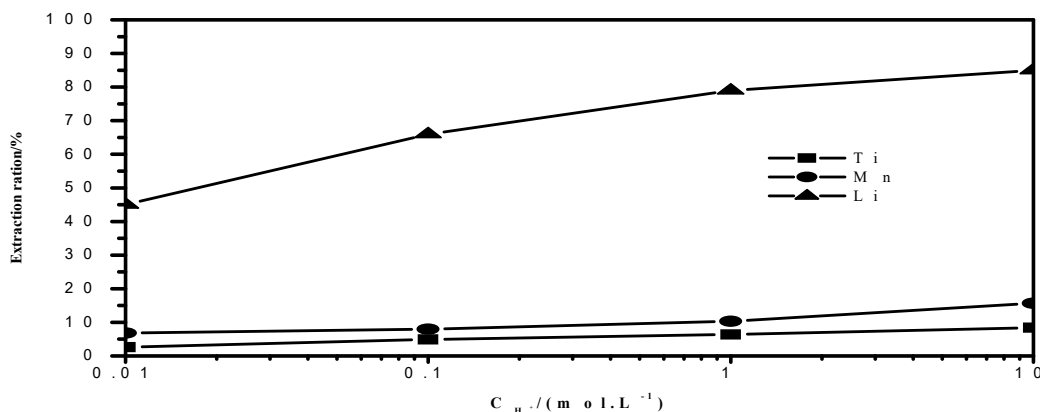


Figure 2. Extraction ration of cations from LiMnTi-800 in HNO_3 solution

Saturation exchange capacity

The relationship between cations radius and its saturated ion exchange capability for alkali is shown in Figure 3. In this diagram, the exchanged capability for Li^+ is the highest, and the Na^+ , K^+ , Rb^+ and Cs^+ decline progressively. The exchanged capability for Li^+ is $9.7 \text{ mmol}\cdot\text{g}^{-1}$. This point the synthesized ion has the higher exchanged capability and better exchanged remembrance capability for Li^+ . There are three effect factors of exchanged saturation capacity for LiMnTi-800(H) , which are listed as follows:

- 1) The Li^+ existed in exchange solution should be removed earlier, because Li^+ will exchange with the vacant space in exchanger once there are too much Li^+ ;
- 2) This experimental research indicates the Li^+ exchanged capability in ion exchange is the highest than its other metal ion in thin solution, which illustrate ion exchanged reaction is more likely to occur in bare ions;
- 3) During the exchange reaction, the Li^+ go into vacant space of exchanger and exchanged with the H^+ surface. Therefore, the compound LiMnTi-800(H) has a higher exchanged capability for Li^+ .

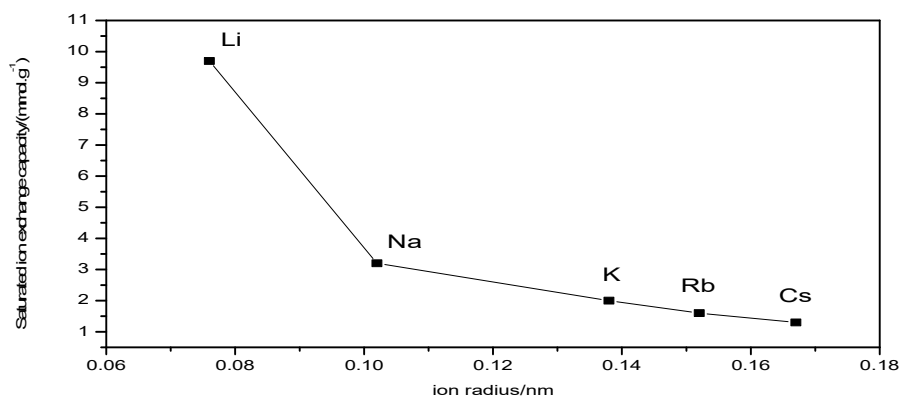


Figure 3. The relationship between cations radius and its saturated ion exchange capability for alkali

Distribution coefficient (K_d)

K_d numerical value can be a characteristic of exchanged selectivity of LiMnTi-800 (H) for correlate ions. In Figure 4, the LiMnTi-800(H) K_d numerical value for alkali ions becomes larger and larger followed by the increasing pH value in the pH experimental range. The LiMnTi-800(H) selective sequence for alkali metal ions are as follows:

$$\text{Li}^+ > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ \quad (1)$$

This shows the LiMnTi-800(H) can be better to choose the Li^+ . This ion-exchange reaction belongs to reversible reaction. In ion-exchanger, the H^+ reacted with other alkali metal ions in solution is as follows (example for Li^+):

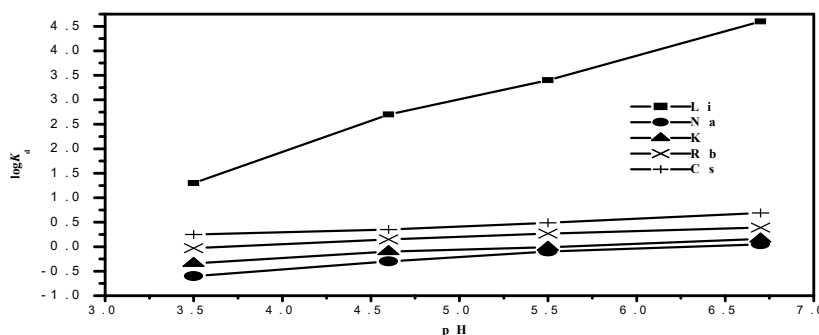


Figure 4. Distribution coefficient of LiMnTi-800 (H) for alkali ions

CONCLUSIONS

$\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$ is an inorganic Li^+ exchanger which has the ion-memory capability. It has better Li^+ electivity; moreover, the structure of lithium-ion sieve preparation is the inverse spinel-type. The exchanged capability of synthesized $\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$ for Li^+ is $9.7 \text{ mmol} \cdot \text{g}^{-1}$. The $\text{Li}_3\text{Mn}_{0.5}\text{Ti}_{0.25}\text{O}_3$ is always used to extract Li^+ from the aqueous solution.

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