

Study of an Inorganic Ion Exchanger $\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$

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The $\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$ was synthesized by a solid state reaction crystallization method, using MgO , MnO_2 and TiO_2 as raw materials. The optimum conditions were obtained by thermal experiment, calcination temperature was at $900\text{ }^\circ\text{C}$, calcination time was 4.5 h. The characterization results showed that the exchange capacity of Li^+ was 8.9 mmol g^{-1} for Li^+ in the solution.

Key Words: Solid state reaction crystallization method, Copound metal oxides, $\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$.

INTRODUCTION

Lithium and its compounds have widely been applied in the aerospace, chemical industry, medicine, air conditioning, thermonuclear reactions and high-energy batteries. The demand of lithium and its compounds will be increased quickly. There are very rich liquid lithium resources in China, It is important to exploit and use the resources of lithium. The methods of extracting lithium from salt water resources, such as salt lake water, the underground brine, salt mother liquid, oil and gas field water have carbonate precipitation method, ion exchange and adsorption method, extraction method. Among which were simple, recovery and selectivity methods of ion exchange and adsorption, they have greater advantages than other methods. It is significance to extraction lithium from a dilute solution by using ion exchange and adsorption methods. This approach is to find an exchange agent with specific selectivity and memory for lithium ion. The appearance of ion memory inorganic materials (ion sieve) became possible direct extracting lithium from the above-mentioned resources. Preparation methods of this exchange agent are sol-gel synthesis, hydrothermal synthesis and high-temperature solid-phase synthesis method^{1,2}. In this paper, inorganic ion exchanger ($\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$) with a spinel structure ion memory was synthesized by solid state reaction crystallization method, which is different the reported in the literatures^{3,4} and its ion-exchange properties were studied.

EXPERIMENTAL

MgO , MnO_2 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 $\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$: The pure ethanol was dropped into a XQM planetary ball mill mixed powder of MgO , MnO_2 and TiO_2 with a $\text{Mg}/\text{Mn}/\text{Ti}$ mole ratio of 1:0.75:0.25 at the condition of constant rate churning. After 8 h, the mixture was mixed completely. The mixture was pressed to tablet by tablet press machine. Then the tablet was heat-treated for 4.5 h at $900\text{ }^\circ\text{C}$ to obtain the Mg-Mn-Ti oxide, the sample was designed as MgMnTiO-900 , whose theoretical formula was $\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$. 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 Mg , Mn and Ti contents were determined by atomic absorption spectrometry.

Cation extraction of MgMnTi oxide and acid modification: Four 0.2 g portions of sample (MgMnTiO-900 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 $25\text{ }^\circ\text{C}$. After 3 days, take the supernatant solution to determine the cation concentration, test its acid proof ability and the extraction ration of Mg^{2+} , Mn^{4+} , Ti^{4+} .

A 5 g portion of sample (MgMnTiO-900) was immersed in a 1 M HNO_3 solution (500 mL) with intermittent shaking in constant temperature water at $25\text{ }^\circ\text{C}$. 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 $900\text{ }^\circ\text{C}$ and acid modified was designated as MgMnTiO-900 (H) . The composition was determined by the method referred and the H content was calculated by subtraction method.

Saturation capacity of exchange: Weigh five 0.5 g portions of MgMnTiO-900 (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. At the same time, do vacant experiment. Last, the inorganic exchanger saturation capacity of exchange for alkali-metal ions obtained by decreasing quantity.

Distribution coefficient (K_d): After weighing four 0.100 g portions of MgMnTiO-900 (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 total concentration of alkali-metal ions was $1.0 \times 10^{-3} \text{ M}$ by adding 9 mL distilled water. After the samples were shaken for 7 days at constant temperature water at 25 °C and were filtered, cation concentrations in each samples were obtained.

RESULTS AND DISCUSSION

Compound and appraisement of $\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$:

The X-ray diffraction pattern of compound metal oxide ($\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$), crystallized was shown in Fig. 1. The structure of compound metal oxide $\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$ crystallized at 900 °C was much perfect.

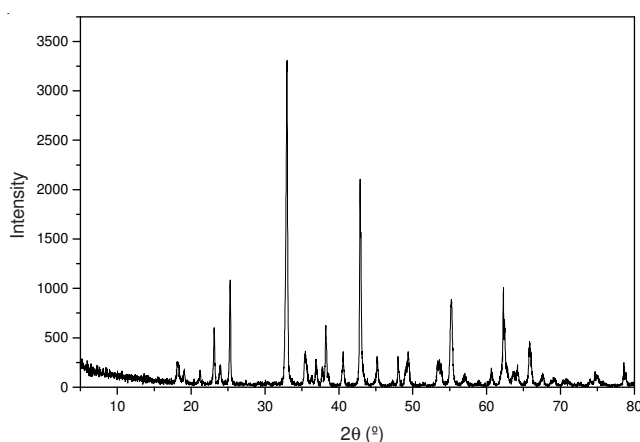


Fig. 1. Powder's X-ray figures of $\text{Mg}_{0.96}\text{Mn}_{0.73}\text{Ti}_{0.24}\text{O}_{2.95}$ crystal

From chemical analysis, the composition of MgMnTiO-900 is $\text{Mg}_{0.96}\text{Mn}_{0.73}\text{Ti}_{0.24}\text{O}_{2.95}$, whose chemical component is basically corresponded with the composition of inverse spinel-type metal oxides.

Cation extraction of compound oxide LiTiO and acid modification: The extraction ratio of Mg^{2+} , Mn^{4+} and Ti^{4+} from MgMnTiO-900 in different concentration HNO_3 solution is shown in Fig. 2. The extractabilities of Mg^{2+} are 29-77 %, Mn^{4+} are 6.0-10.2 % and Ti^{4+} are 2.6-8.0 % (Fig. 2). Those indicate that the extractabilities of Mg^{2+} are higher than those of Mn^{4+} and Ti^{4+} when exchanger was immersed in 1 M acid solution, corresponding with the exchanger condition was better (1 N, Mg^{2+} 72 %, Mn^{4+} 8.2 %, Ti^{4+} 6.2 %).

The analysis indicate the composition of MgMnTiO-900 (H) was $\text{H}_{1.38}\text{Mg}_{0.27}\text{Mn}_{0.69}\text{Ti}_{0.23}\text{O}_{2.89}$, whose component of 72 %

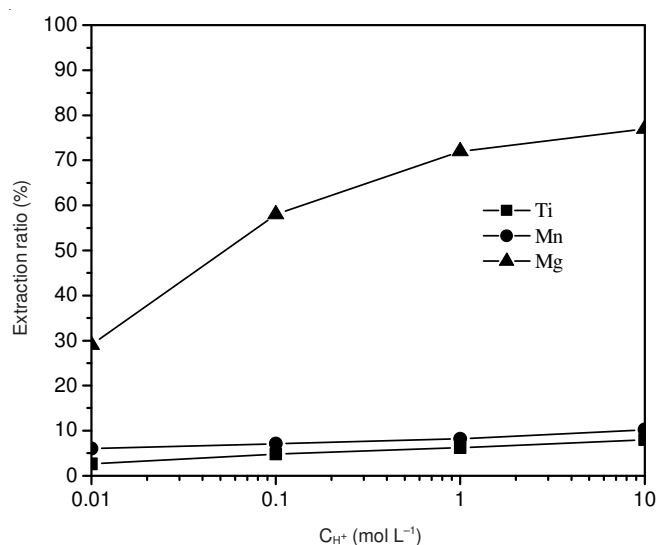


Fig. 2. Extraction ratio of cations from MgMnTiO-900 in nitric acid solution

Mg^{2+} transformed to H^+ compared with the composition $\text{Mg}_{0.96}\text{Mn}_{0.73}\text{Ti}_{0.24}\text{O}_{2.95}$ before acid-treated. Then the specific Mg^{2+} 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 MgMnTiO-900 (H) for alkali was shown in Fig. 3. The capacity of exchange for Li^+ was much higher than those for other alkali ions. The capacity for Li^+ is 8.9 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 MgMnTiO-900 (H) are: (1) The Li^+ in exchange solution must be removed previously, because Li^+ exchanged with exchanger vacancy site when existing too much Li^+ ; *2) 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; (3) 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, MgMnTiO-900 (H) has a higher exchange capacity for Li^+ .

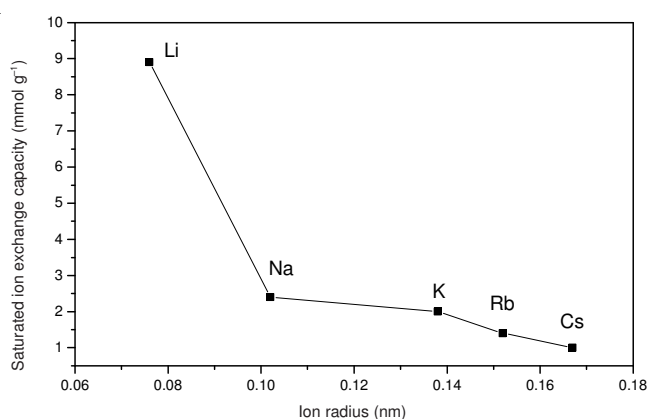


Fig. 3. Relation between ion radius and saturated ion exchange capacity of MgMnTiO-900(H) for alkali ions

Distribution coefficient (K_d): K_d values can be the token of exchange selectivity of MgMnTiO-900 (H) for correlate ions. Shown in Fig. 4, K_d values of MgMnTiO-900 (H) for alkali ions are larger and larger with an increase pH over the pH region studied. The selectivity sequence of MgMnTiO-900 (H) for alkali metal ions as follows:



It indicates that MgMnTiO-900 (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^+):



Conclusion

The comprehensive results indicate that the $\text{MgMn}_{0.75}\text{Ti}_{0.25}\text{O}_3$ of inverse 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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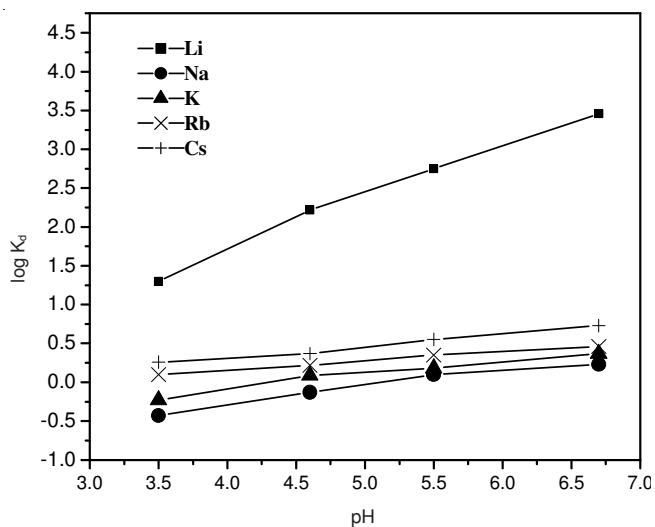


Fig. 4. Distribution coefficient of MgMnTiO-900(H) for alkali ions