



Synthesis of $Mg_{1.5}MnTi_{0.25}O_4$ and Its Selectivity to Li^+ Exchange

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The ion-exchanger $Mg_{1.5}MnTi_{0.25}O_4$ of inverse 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. $Mg_{1.5}MnTi_{0.25}O_4$ was characterized by X-ray diffraction method. The acid treatment of $Mg_{1.5}MnTi_{0.25}O_4$ causes Mg^{2+} extraction ratio to change from 30 to 78 %, while dissolution of Ti^{4+} is less than 8 %. This inorganic ion-exchanger ($Mg_{1.5}MnTi_{0.25}O_4$) has the saturation capacity of exchange for Li^+ higher than those for other alkali ions. The saturation capacity of exchange for Li^+ reaches to 10.9 mmol/g, $MgMnTi$ -900(H) has a higher selectivity of ion exchange for Li^+ than for other alkali ions.

Key Words: Inverse spinel type complex oxide, Lithium, Ion exchange, $MgMnTi$ -900.

INTRODUCTION

The ocean is called the "treasure house of resources". The ocean has 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 *ca.* 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 discussion is about the synthesis, structure and ion exchange of the Mg-Mn-Ti composite oxide inorganic ion exchanger of $Mg_{1.5}MnTi_{0.25}O_4$. The experimental result have been proved that the inorganic material has good selectivity and higher capacity of exchange for Li^+ in solution.

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 identification of $Mg_{1.5}MnTi_{0.25}O_4$: The pure ethanol was dropped into a XQM planetary ball mill mixed powder of MgO , MnO_2 and TiO_2 with a Mg/Mn/Ti mole

ratio of 1.5:1:0.25 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 900 °C to obtain the Mg-Mn-Ti oxide, the sample was designed as $MgMnTiO$ -900, whose theoretical formula was $Mg_{1.5}MnTi_{0.25}O_4$. 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 Mg, Mn and Ti contents were determined by atomic absorption spectrometry.

Cation extraction of $MgMnTi$ oxide and acid modification: Four 0.200 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 °C. After 3 days, take the supernatant solution to determine the cation concentration, test its acid proof ability and the extraction ratio 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 °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 °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 decrease 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 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 appraisalment of $\text{Mg}_{1.5}\text{MnTi}_{0.25}\text{O}_4$: The X-ray diffraction pattern of compound metal oxide ($\text{Mg}_{1.5}\text{MnTi}_{0.25}\text{O}_4$), crystallized was shown in Fig. 1. The structure of compound metal oxide $\text{Mg}_{1.5}\text{MnTi}_{0.25}\text{O}_4$ crystallized at 900 °C was much perfect.

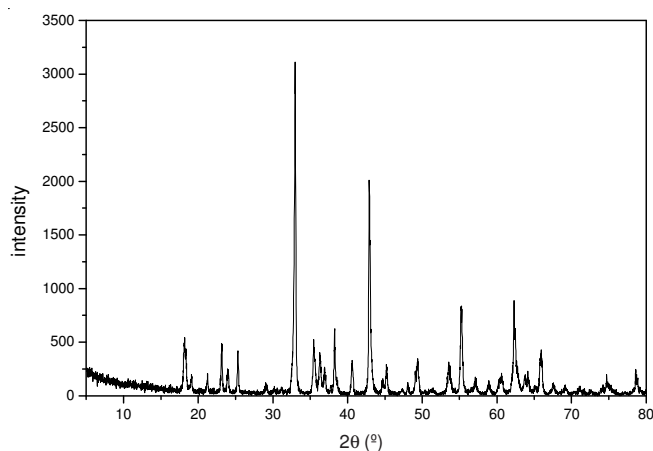


Fig. 1. Powder's X-ray figures of $\text{Mg}_{1.46}\text{Mn}_{0.97}\text{Ti}_{0.24}\text{O}_{3.96}$ crystal

From chemical analysis, the composition of MgMnTiO-900 is $\text{Mg}_{1.46}\text{Mn}_{0.97}\text{Ti}_{0.24}\text{O}_{3.96}$, whose chemical component is basically corresponded with the composition of inverse spinel-type metal oxides.

Cation extraction of compound oxide MgMnTiO 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 30-78 %, Mn^{4+} are 6.5-10.3 % and Ti^{4+} are 2.7-8.0 % (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+} 8.9 %, Ti^{4+} 6.4 %).

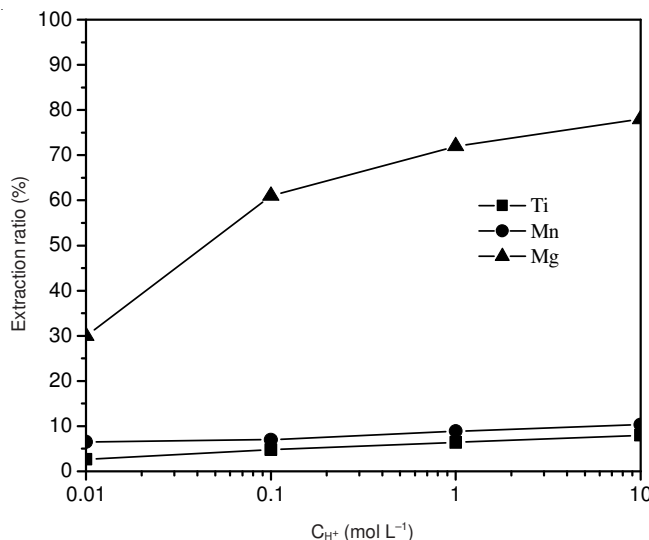


Fig. 2. Extraction ration of cations from MgMnTiO-900 in nitric acid solution

The analysis indicate the composition of MgMnTiO-900 (H) was $\text{H}_{2.10}\text{Mg}_{0.41}\text{MnTi}_{0.25}\text{O}_4$, whose component of 72 % Mg^{2+} transformed to H^+ compared with the composition $\text{Mg}_{1.46}\text{Mn}_{0.79}\text{Ti}_{0.22}\text{O}_{3.57}$ 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 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 (Fig. 3). The capacity for Li^+ is 10.9 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^+ exchange 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^+ .

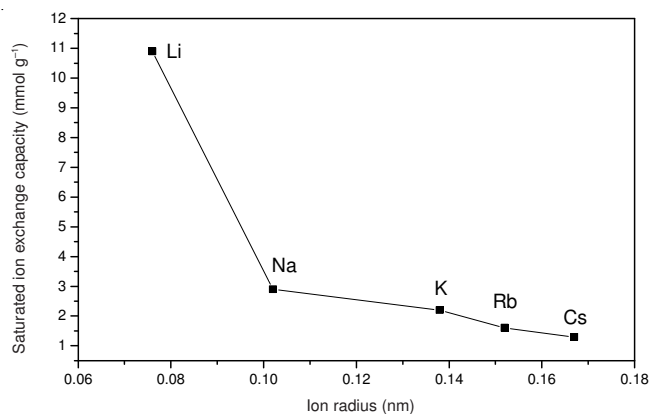


Fig. 3. Relation between ion radius and saturated ion exchange capacity of MgMnTiO-900 (H) for alkali ions

Distribution coefficient (K_d): K_d values can be the token of exchange selectivity of $MgMnTiO-900$ (H) for correlate ions. Fig. 4 showed that the 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:

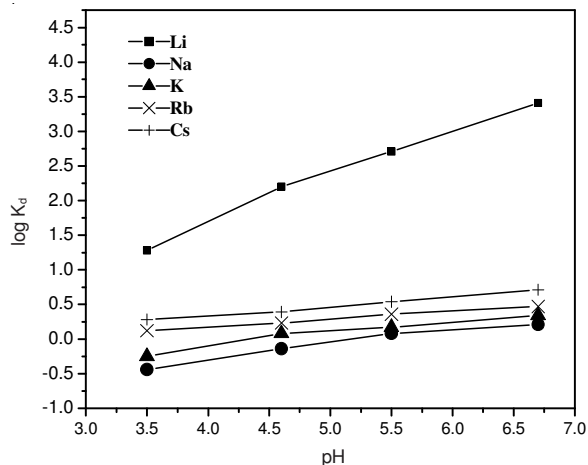


Fig. 4. Distribution coefficient of $MgMnTiO-900$ (H) for alkali ions

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 $Mg_{1.5}MnTi_{0.25}O_4$ 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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