Synthesis of \( \text{Mg}_{1.5}\text{Mn}_{0.75}\text{Ti}_{0.5}\text{O}_4 \) and Its \( \text{Li}^+ \) Extraction/Insertion Reaction in the Aqueous Phase

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INTRODUCTION

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. Apart from that, it appears the fine substance in dealing with nuclear waste, gathering and separating of metal ions and chromatogram analysis1,2. In this paper, the solid state reaction crystallization method was used to synthesize the \( \text{Mg}_{1.5}\text{Mn}_{0.75}\text{Ti}_{0.5}\text{O}_4 \) of inverse spinel-type oxide, whose composition and structure are different from those in literature3,4. The experimental result have proved that the inorganic material has good selectivity and higher capacity of exchange for \( \text{Li}^+ \) in the solution removed \( \text{Li}^+ \) previously. Moreover, the cost is low and its application prospect is significant.

EXPERIMENTAL

\( \text{MgO}, \, \text{MnO}_2 \) and \( \text{TiO}_2 \) 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; tube furnace.

Synthesis and identification of \( \text{Mg}_{1.5}\text{Mn}_{0.75}\text{Ti}_{0.5}\text{O}_4 \): The pure ethanol was dropped into a XQM planetary ball mill mixed powder of \( \text{MgO}, \, \text{MnO}_2 \) and \( \text{TiO}_2 \) with a \( \text{Mg}/\text{Mn}/\text{Ti} \) mole ration of 1.5:0.75:0.5 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 900 °C to obtain the \( \text{Mg-Mn-Ti} \) oxide, the sample was designed as \( \text{MgMnTiO-900} \), whose theoretical formula was \( \text{Mg}_{1.5}\text{Mn}_{0.75}\text{Ti}_{0.5}\text{O}_4 \). Then it was been analyzed by X-ray diffraction and compared to literature3,4.

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 \( \text{MgMnTi} \) oxide and acid modification: Four 0.200 g portions of sample (\( \text{MgMnTiO}_{900} \) oxides) were immersed in a \( \text{HNO}_3 \) 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 proofability and the extraction ration of \( \text{Mg}^{2+}, \, \text{Mn}^{4+}, \, \text{Ti}^{4+} \).

A 5 g portion of sample (\( \text{MgMnTiO}_{900} \)) was immersed in a 1 M \( \text{HNO}_3 \) solution (500 mL) with intermittent shaking in constant temperature water at 25 °C. After 7 days, remove the supernatant solution and add new \( \text{HNO}_3 \) solution. Repeating that for twice, then the initial sample was transformed to \( \text{H} \)-type sample, washed with water and air-dried. The sample obtained by thermal crystallized at 900 °C and acid modified was designated as \( \text{MgMnTiO-900} \) (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 \( \text{MgMnTiO-900} \) (H), then each portion was immersed in a 0.1 M solution (10 mL), containing \( \text{Li}^+ \), \( \text{Na}^+ \), \( \text{K}^+ \), \( \text{Rb}^+ \) and \( \text{Cs}^+ \), respectively, diluted to 100 mL, shaken in constant temperature water at 25 °C. After saturation exchanging (namely, after 10 days by literature3,4 the solutions were filtered by
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-metals 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 ºC and were filtered, cation concentrations in each samples were obtained.

RESULTS AND DISCUSSION

Compound and appraisal of Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀:
The X-ray diffraction pattern of compound metal oxide (Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀), crystallized was shown in Fig. 1. The structure of compound metal oxide Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ crystallized at 900 ºC was much perfect.

We know from chemical analysis, the composition of Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ is Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀, whose chemical component is basically corresponded with the composition of inverse spinel-type metal oxides.

Cation extraction of compound oxide Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ and acid modification: The extraction ratio of Mg²⁺, Mn⁴⁺ and Ti⁴⁺ from Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ in different concentration HNO₃ solution is shown in Fig. 2. The extractabilities of Mg²⁺ are 32-78 %, Mn⁴⁺ are 5.7-10.1 % and Ti⁴⁺ are 2.6-8.5 %, respectively (Fig. 2). Those indicate that the extractabilities of Mg²⁺ are higher than those of Mn⁴⁺ and Ti⁴⁺ when exchange was immersed in 1 M acid solution, corresponding with the exchange condition was better. (1 N, Mg²⁺ 73 %, Mn⁴⁺ 8.8 %, Ti⁴⁺ 6.6 %).

The analysis indicate the composition of Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ (H) was H₂₋₄Mg₀₋₁Mn₀₋₁Ti₄₋₅O₄₋₆, whose component of 73 % Mg²⁺ transformed to H⁺ compared with the composition Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ 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 Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ (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 11.1 mmol g⁻¹ (Fig. 3). It prove 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 Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ (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 showed 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 absorbed by the surface of compound oxide Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀. Therefore, Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ (H) has a higher exchange capacity for Li⁺.

Distribution coefficient (Kₐ): Kₐ values can be the token of exchange selectivity of Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ (H) for correlate ions. Fig. 4 showed the Kₐ values of Mg₂₋₄Mn₄₋₅Ti₆₋₇O₁₉₋₂₀ (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:

\[
\text{Li}^+ > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+
\]

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$^+$):

\[
\text{E-2H} + 2\text{Li}^+ \leftrightarrow \text{E-2Li} + 2\text{H}^+
\]

Conclusion

The comprehensive results indicate that the Mg$_{1.5}$Mn$_{0.75}$Ti$_{0.5}$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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