SYNTHESIS AND ABSORPTION PROPERTIES OF NOVEL NA SPECIFIC ADSORBENT \( \text{Li}_{1-x}\text{La}_x\text{Zr}_2\text{Al}_3(\text{PO}_4)_3 \)

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ABSTRACT

A novel kind of adsorbent \( \text{Li}_{1-x}\text{La}_x\text{Zr}_2\text{Al}_3(\text{PO}_4)_3 \) was synthesized by solid state reaction method. The influence of the content of doping lanthanum on the adsorbent \( \text{Li}_{1-x}\text{La}_x\text{Zr}_2\text{Al}_3(\text{PO}_4)_3 \) was investigated by XRD and FTIR spectra while the morphology of powders was observed by SEM. The investigation of the adsorption properties showed that the adsorbent can selectively adsorb sodium with the adsorption capacity of 49.83 mg/g. The optimum conditions of adsorption are at pH 10.0–11.0 in LiCl solution.

Keywords: LiCl, \( \text{Li}_{1-x}\text{La}_x\text{Zr}_2\text{Al}_3(\text{PO}_4)_3 \), adsorbent, separation.

INTRODUCTION

Lithium chloride is an industrial raw material, from which lithium compounds and in particular metallic lithium are produced. To make further processing of the lithium chloride more economic and efficient, it is very necessary to provide the raw material as pure as possible. The presence of very small quantities of sodium in the lithium metal will make it highly reactive and much different in properties than purity lithium metal. So as the raw material of LiCl it is required in low content of Na.

The ordinary separation method is to extract sodium with isopropanol\(^1\), which not only consumes substantial organic solvent, but also is harmful to environment. The adsorption method is briefly and feasible in theory, but the synthesis of an applicable adsorbent is a big problem. In the decades, antimonic and polyantimonic acid have been studied in the field\(^2\), but it failed to practice because of the high cost. At present, to meet the rapidly increasing demand on lithium chloride, especially the high pure lithium chloride, it is urgent to remove Na\(^+\) in the produce of the high pure lithium chloride.

NASICON(Acronym of natrium superionic conductor) materials present interesting sensitive and selective properties against alkaline cations due to their structure. \( \text{Li}_{1+x}\text{Al}_x\text{Ti}_{1-x}(\text{PO}_4)_3 \) possesses the NASICON-type structure, is especially good candidates to determine alkaline ions concentrations in solution or to separate monovalent cations from a mixture of multivalent ions\(^3\)

\( \text{Li}_{1+x}\text{Al}_x\text{Ti}_{1-x}(\text{PO}_4)_3 \) composed of both \( \text{MO}_3 \) octahedra and \( \text{PO}_4 \) tetrahedra which are linked by their corners to form a opened-three-dimension (3D) network structure. The resulted structure consists of Type I sites(octahedral O-coordination) and Type II sites(10-fold O-coordination) for the mobile Li ions to occupy. Li\(^+\) ions move from one site to another passing through bottlenecks defined by the anionic skeleton \( [\text{Al}_x\text{Ti}_{1-x}(\text{PO}_4)_3]^{1.6+}\).

Zr(4d series) and Ti(3d series) which belongs to same group of elements in the periodic table, have similar chemical properties. Lanthanide series are defined by the anionic skeleton \( [\text{Al}_x\text{Ti}_{1-x}(\text{PO}_4)_3]^{1.6+} \).

RESULTS AND DISCUSSION

2 Characterization and Measurements of adsorption capacity

2.1 DSC-TGA

The thermal analysis (DSC-TGA) was carried out by employing a TA SDT Q600. The samples were heated to 1000 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

2.2 XRD

The X-ray diffraction(XRD) was performed at room temperature on a Rigaku D/max-3B X-Ray diffractometer, the X-ray beam was nickel-filtered Cu K\(\alpha\) (\(\lambda=0.15406 \text{ nm}\)) radiation operated at 40 kV and 30 mA; and the data were collected from 3° to 80°(2\(\theta\)) at a scanning rate of 5 °/min.

2.3 FTIR

The Fourier transform infrared(FTIR) spectra were recorded on a Thermo Nicolet Nexus in the wave number range of 4000–400 cm\(^{-1}\). Care was taken to press all the KBr pellets under the same conditions to minimize any effect of pressure on peak frequencies for the power samples.

2.4 Measurements of adsorption capacity

1.0 g diffraction patterns of \( \text{Li}_{1-x}\text{La}_x\text{Zr}_2(\text{PO}_4)_3 \) samples were added to 100 g LiCl solution contained 0.06% Na\(^+\). The concentration of Na\(^+\) in solution was measured after stirring the solution for 10 h at pH 11.0. The adsorption capacity of \( \text{Li}_{1-x}\text{La}_x\text{Zr}_2(\text{PO}_4)_3 \) samples was carried out at different pH value and different content of doping lanthanum.

EXPERIMENTAL

1 Preparation of \( \text{Li}_{1-x}\text{La}_x\text{Zr}_2(\text{PO}_4)_3 \) with Different amounts of Dopant

\( \text{Li}_{1-x}\text{La}_x\text{Zr}_2(\text{PO}_4)_3 \) \((x=0.0–1.0)\) was prepared by solid state reaction of \( \text{Li}_2\text{CO}_3 (\text{A. R.}), \text{ZrO}_2 (\text{A. R.}), \text{La}_2\text{O}_3 (\text{A. R.}), \text{NH}_3\cdot\text{H}_2\text{O} (\text{A. R.}), \text{CH}_3\text{OH}(\text{A. R.}) \). The starting materials were weighed in stoichiometric amounts and homogenized using a mixer. The mixture was put in a tubular furnace and had been heated for 6 h at 600 °C to decompose the oxalate and the phosphate. The powder was cooled down to room temperature and then pressed into \( \Phi 10 \text{ mm} \) pellets under 20 MPA. After grinding and homogenization, the mixture was transferred to the furnace and annealed at 1000 °C for 20 h.

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Fig. 1 DSC-TGA curves of the raw material

The phase evolution of diffraction patterns \( \text{Li}_{1-x}\text{La}_x\text{Zr}_2(\text{PO}_4)_3 \) were studied by the XRD analysis (Fig. 2). The substitution of La\(^3+\) for Zr\(^4+\) was tried
synthetically to observe the change of the crystalline structure. The LiZr(PO₄)₃ structure was retained in the solid solution range at x<0.4. It was indexed in the rhombohedral system with lattice: rhomb-centered, space group R3c and the cell parameters: a = 0.88077 nm, b = 0.88077 nm, c = 2.2715 nm, α = 90°, β = 90°, γ = 120°. It showed that trifle La⁺ dopant did not affect the structure of the material. Some additional diffraction peaks appeared in the XRD patterns when x is above 0.4.

Fig. 2 The XRD patterns of Liₓ₋₀.₄₋ₓLaₓLa₄₋ₓZrₓ₋₀.₄₋ₓ(PO₄)₃ samples
Molar fraction of dopants: a. x = 1; b. x = 0.8; c. x = 0.6; d. x = 0.4; e. x = 0.2; f. x = 0.
The IR spectra of diffraction patterns of Liₓ₋₀.₄₋ₓLaₓLa₄₋ₓZrₓ₋₀.₄₋ₓ(PO₄)₃ are shown in Fig.3. The shape of IR spectrum weakened along with the gradual augmentation of La⁺. It showed that the augmentation of La⁺ led to the aberration of Liₓ₋₀.₄₋ₓLaₓLa₄₋ₓZrₓ₋₀.₄₋ₓ(PO₄)₃ crystal lattice and the lessening of the component of crystalloid.

Fig.3 FTIR spectra of Liₓ₋₀.₄₋ₓLaₓLa₄₋ₓZrₓ₋₀.₄₋ₓ(PO₄)₃
Molar fraction of dopants: a. x = 0; b. x = 0.2; c. x = 0.4; d. x = 0.6; e. x = 0.8; f. x = 1.
Keeping other variables constant (Table 1), the adsorption capacity of Liₓ₋₀.₄₋ₓLaₓLa₄₋ₓZrₓ₋₀.₄₋ₓ(PO₄)₃ towards Na⁺ was measured at different pH values. It was found that the adsorption capacity was quantitatively retained in the pH range of 10.0–11.0. So the optimum pH value of adsorption was from 10.0 to 11.0 in LiCl solution.

Table 1 Influence of pH on the adsorption capacity Na⁺ of Liₓ₋₀.₄₋ₓLaₓLa₄₋ₓZrₓ₋₀.₄₋ₓ(PO₄)₃

<table>
<thead>
<tr>
<th>pH</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adsorption capacity (mg·g⁻¹)</td>
<td>1.20</td>
<td>8.37</td>
<td>15.41</td>
<td>40.25</td>
<td>49.83</td>
</tr>
</tbody>
</table>

The adsorption capacity of LiZr(PO₄)₃ samples was shown in Table 2. The adsorption capacity of LiZr(PO₄)₃ to Na⁺ was 5.16 mg/g and the La⁺ dopant considerably improved its specific adsorption capacity to Na⁺. When x = 0.4, the adsorption capacity reached the maximum value of 49.83 mg/g. So the optimum dopant quantity of La⁺ was x = 0.4.

Table 2 The adsorption capacity of Liₓ₋₀.₄₋ₓLaₓLa₄₋ₓZrₓ₋₀.₄₋ₓ(PO₄)₃

<table>
<thead>
<tr>
<th>x</th>
<th>Adsorption capacity (mg·g⁻¹)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.15</td>
<td>5.67</td>
</tr>
<tr>
<td>0.2</td>
<td>41.40</td>
<td>39.13</td>
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<tr>
<td>0.4</td>
<td>49.05</td>
<td>51.77</td>
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<td>0.6</td>
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<tr>
<td>0.8</td>
<td>15.94</td>
<td>19.40</td>
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<tr>
<td>1.0</td>
<td>11.67</td>
<td>10.99</td>
</tr>
</tbody>
</table>

CONCLUSION

In this study, we synthesized a novel kind of adsorbent Liₓ₋₀.₄₋ₓLaₓLa₄₋ₓZrₓ₋₀.₄₋ₓ(PO₄)₃ by solid state reaction method. The trifle La⁺ dopant did not affect the structure of the material but considerably improved its specific adsorption capacity towards Na⁺. It could be used to remove Na⁺ from lithium chloride. The results of adsorbing test showed that its exchange capacity was high with the maximum value of 49.83 mg/g at x = 0.4, pH = 10.0–11.0. That method was a simpler and more convenient way to remove Na⁺ from lithium chloride solution.

REFERENCES AND ACKNOWLEDGMENTS

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