SYNTHESIS AND ADSORPTION PROPERTIES OF NOVEL NA SPECIFIC ADSORBENT $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$

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ABSTRACT

A novel kind of adsorbent $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ was synthesized by solid state reaction method. The influence of the content of doping lanthanum on the adsorbent $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ 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, $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$, 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 isopropanol¹, which not only consumes substantive organic solvent, but also is serious harm 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, antimonite and polyantimonite acid have been studied in the field², 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. $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ 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^{3,4}.

$\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ composed of both MO_6 octahedra and PO_4 tetrahedra which are linked by their corners to form an 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 bottle-necks defined by the anionic skeleton $[\text{AlTi}_2(\text{PO}_4)_3]^{(1-x)-}$.

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 widely used in the field of catalysts, functional materials and new material⁵. The valence of La and Al mainly is +3, Then, the attempt was done in this paper to improve the adsorption performance by substitute La and Zr for Al and Ti.

The results showed that $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ show higher absorption capacities towards Na^+ . The exchange capacity of $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$ was 49.83 mg/g, which is four times of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$. Compared with other methods, the novel Na specific adsorbent of $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ described here is a simpler and more convenient way to remove Na^+ from LiCl solution which suggest the promising application.

EXPERIMENTAL

1 Preparation of $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ with Different amounts of Dopant

$\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ ($x=0.0\sim1.0$) was prepared by solid state reaction of Li_2CO_3 (A. R.), ZrO_2 (A. R.), La_2O_3 (A. R.), $\text{NH}_4\text{H}_2\text{PO}_4$ (A. R.), $\text{C}_6\text{H}_8\text{O}_7$ (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 under Φ 10 mm pellets under 20 MPa. After grinding and homogenization, the mixture was transferred to the furnace and annealed at 1000 °C for 20 h.

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 $\text{Cu K}\alpha$ ($\lambda=0.15406$ nm) radiation operated at 40 kV and 30 mA; and the data were collected from 3° to 80° (2 θ) 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 $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ samples were added to 100 g LiCl solution contained 0.06% Na^+ . The concentration of Na^+ in solution is measured after stirring the solution for 10 h at pH 11.0. The adsorption capacity of diffraction patterns of $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$ samples was carried out at different pH value and different content of doping lanthanum.

RESULTS AND DISCUSSION

Fig. 1 shows DSC-TGA curves of the raw material. There are four endothermic peaks at 121 °C 204 °C 310 °C and 341 °C in DSC curves. TG curve revealed the mass loss of 24.95% which occurred at 20 °C to 600 °C, while no change in weight was found from 600~1000 °C. The following reaction can be expected to have mass loss of 24.52%:

Fig. 1 DSC-TGA curves of the raw material

The phase evolution of diffraction patterns $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ 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 $\text{LiZr}_2(\text{PO}_4)_3$ structure was retained in the solid solution range at $x \leq 0.4$. It was indexed in the rhombohedral system with lattice: rhomb-centered, space group $R\bar{3}c$ and the cell parameters: $a=0.88077$ nm, $b=0.88077$ nm, $c=2.2715$ nm, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=120^\circ$. It showed that trifluoride La^{3+} 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 $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ 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 $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ are shown in Fig.3. The shape of IR spectrum weakened along with the gradual augmentation of La^{3+} . It showed the augmentation of La^{3+} led to the aberration of $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ crystal lattice and the lessening of the component of crystalloid^{6,7}.

Fig.3 FTIR spectra of $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$

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 $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$ 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 $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$

pH	5	7	9	10	11	12
Adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$)	1.20	8.37	15.41	40.25	49.83	30.06

The adsorption capacity of diffraction patterns of $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ samples was shown in Table 2. The adsorption capacity of $\text{LiZr}_2(\text{PO}_4)_3$ to Na^+ was 5.16 mg/g and the La^{3+} 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^{3+} was $x=0.4$.

After adding La in $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ crystal structure, Zr was replaced by La and Li, which produced negative charge among crystal layers and made La and Li becoming two active centers and benefited to adsorb some cation. However, the excessive La would destroy the structure of $\text{LiZr}_2(\text{PO}_4)_3$ with forming Li_3PO_4 and LaPO_4 , while Na can not be adsorbed. The idiographic mechanism needs to be further studied.

Table 2 The adsorption capacity of diffraction patterns of $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$

x	Adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$)				
	1	2	3	4	Average
0	4.15	5.67	4.39	6.10	5.16
0.2	41.40	39.13	39.71	40.78	40.27
0.4	49.05	51.77	50.74	47.63	49.83
0.6	36.08	38.26	36.83	35.82	36.75
0.8	15.94	19.40	18.72	17.59	17.93
1.0	11.67	10.99	8.46	10.12	10.56

CONCLUSION

In this study, we synthesized a novel kind of adsorbent $\text{Li}_{1-x}\text{La}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ by solid state reaction method. The trifluoride La^{3+} 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 $x=0.4$, $\text{pH}=10.0\sim 11.0$. That method was a simpler and more convenient way to remove Na^+ from lithium chloride solution.

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