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Synthesis and Absorption Properties of New Na Specific Adsorbent $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$

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Abstract: A new kind of adsorbent $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ was synthesized by solid state reaction method. The influence of the content of doping aluminum on the adsorbent $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ was investigated by XRD, 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 11.76 mg/g. The optimum conditions of adsorption are at pH 10.0-11.0 in LiCl solution.

Keywords: $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, adsorbent, separation.

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[1,2]. 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, which not only consumes substantive organic solvent, but also is serious harm to environment. In this work, we report the synthesis of the adsorbent $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ by solid state reaction method. It is found that they show high absorption capacities towards Na^+. Compared with the other methods, the new Na specific adsorbent $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ described here is a simpler and more convenient way to remove Na^+ from LiCl solution and shows the favorable prospective to its application.

Experimental

$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (x=0.0~1.0) was prepared by solid state reaction of Li_2CO_3(A. R.), TiO_2(C. R.), Al_2O_3(A. R.), $NH_4H_2PO_4$(A. R.), C_6H_{14}(A. R.). The starting materials were weighed in stoichiometric amounts and homogenized with a mixer. The mixture was put in a tubular furnace and had been heated for 6 h at 500 °C to decompose the oxalate and the phosphate. The powder was cooled down to room temperature and then pressed

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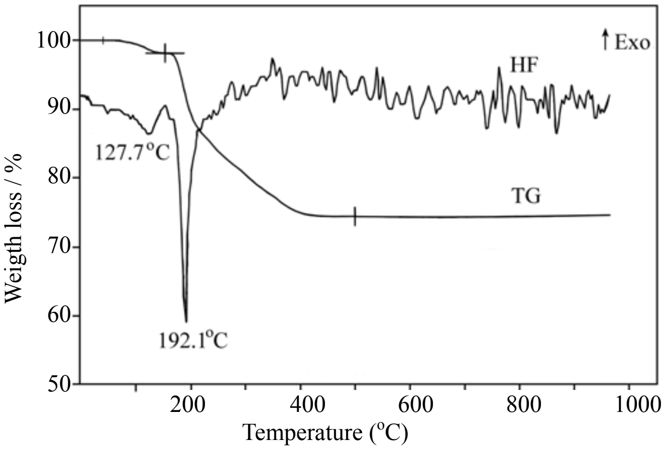
into *Φ* 10 mm pellets under 20 MPa. After grinding and homogenization, the mixture was transferred to the furnace and annealed at 1000 °C for 20 h. TG-DTA thermal analysis was carried out on SETARAM TG/DTA92 with the heating temperature from 20 to 1000 °C at 5 °C/min in N_2. XRD patterns for all the samples were measured by Rigaku D/max-3B X-ray Diffractometer[3]. The morphology of the samples was observed by JEOL JSM-5600LV SEM.

Results and Discussion

Figure 1 shows TG/DTA curves of the raw material. There are two endothermic peaks at 127.7 °C and 192.1 °C in DTA curves. TG curve revealed the weight loss of 28.1%, which occurred at 20 °C to 500 °C, while no change in weight was found from 500-1000 °C. The following reaction can be expected to have weight loss of 28.4%:

$$(1+x)Li_2CO_3+xAl_2O_3+(4-2x)TiO_2+6NH_4H_2PO_4 \rightarrow$$
$$2Li_{1+x}Al_xTi_{2-x}(PO_4)_3+9H_2O+6NH_3+(1+x)CO_2$$

Figure 1 TG/DTA curves of the raw material



The phase evolution of diffraction patterns $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ were studied by the XRD analysis (shown in **Figure 2**).

The substitution of Al^{3+} for Ti^{4+} was tried synthetically to observe the change of the crystalline structure. The $LiTi_2(PO_4)_3$ structure was retained in the solid solution range at $x<0.6$. It was indexed in the rhombohedral system with lattice: rhomb-centered, space group $R\bar{3}c$ and the cell parameters: a=0.8518 nm, b=0.8518 nm, c=2.087 nm, α=90 °, β=90 °, γ=120 °. It showed that trifle Al^{3+} dopant did not affect the structure of the material. Some additional diffraction peaks appeared in the XRD patterns when x was above of 0.6.

Figure 3 showed the microspheres for $LiTi_2(PO_4)_3$(a) and $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$(b). The results showed they are highly dispersive particles with diameters ranged at 60-80 μm.

Figure 2 XRD of diffraction patterns of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ samples

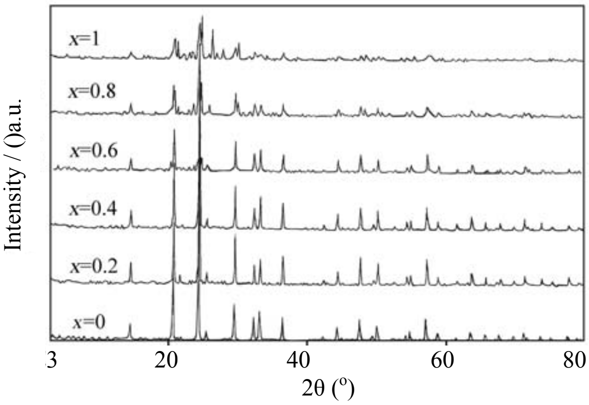


Figure 3 SEM photos of diffraction patterns of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$

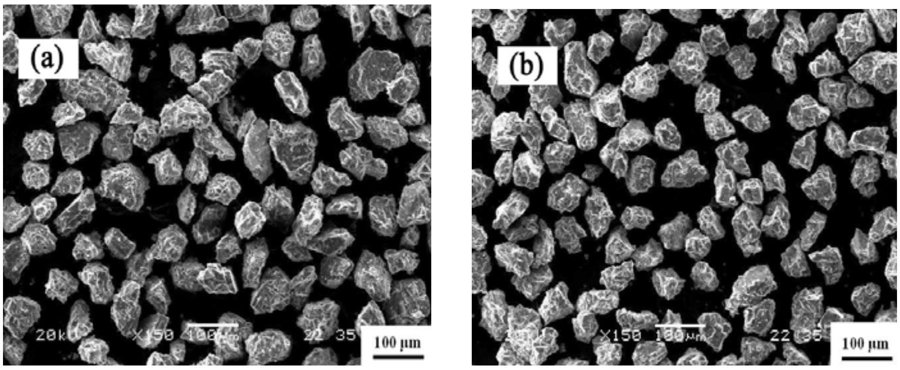


Table 1 Influence of pH on the adsorption capacity Na^+ of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$

pH	5	7	9	10	11	12
Adsorption capacity (mg/g)	0.20	2.37	4.13	11.25	11.76	10.39

Keeping other variables constant (**Table 1**), the adsorption capacity of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ 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.

5.0 g diffraction patterns of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ 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 $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ samples was shown in **Table 2**. It was obvious that $LiTi_2(PO_4)_3$ could not adsorpt Na^+ and the Al^{3+} dopant considerably improved its specific adsorption capacity to Na^+. When x=0.4, the adsorption capacity reached the maximum value of 11.76 mg/g. So the optimum dopant quantity of Al^{3+} was x=0.4. The adsorbent could regenerate easily with 0.1 mol/L HCl solution and its activity and selectivity did not change after 10 cycles, which showed that the stability of the adsorbent was excellent.

After adding Al in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ crystal structure, Ti was replaced by Al and Li, which produced negative charge among crystal layers and made Al and Li becoming two active centers and to benefit to adsorb some cation. However, the excessive Al would destroy the structure of $LiTi_2(PO_4)_3$ with forming Li_3PO_4 and $AlPO_4$, while Na could not be adsorbed. The idiographic mechanism needs to be further studied.

Table 2 The adsorption capacity of diffraction patterns of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$

x	Adsorption capacity (mg/g)				
	1	2	3	4	Average
0	0.24	0.34	0.18	0.46	0.31
0.2	7.58	8.00	7.84	7.36	7.70
0.4	11.78	11.70	11.80	11.74	11.76
0.6	8.58	9.10	8.76	8.52	8.74
0.8	4.24	5.16	4.98	4.68	4.77
1.0	3.46	3.12	2.54	2.88	3.00

Conclusion

In this study, we synthesized a new kind of adsorbent $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ by solid state reaction method. The trifle Al^{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 11.76 mg/g at x=0.4, pH=10.0~11.0. The adsorption capacity could almost be recovered by regenerating it with 0.1 mol/L HCl solution. That method was a simpler and more convenient way to remove Na^+ from lithium chloride solution.

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