



Synthesis and Properties of Novel Na⁺ Ion Exchanger

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A novel sodium specific kind of ion exchanger $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$ was synthesized by solid state reaction method. The sample was characterized by X-ray diffraction (XRD), infrared spectrum (FTIR) and scanning electron microscope (SEM). The investigation of the ion exchange properties showed that its exchange capacity is very high, even reach 41.3 mg/g and it can be used to remove Na^+ from lithium chloride. The Na/Li ion exchange reaction rate increased obviously for $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$ with increasing temperature and the Na/Li ion exchange kinetics process in lithium chloride solution could be represented approximately by the equation of JMAK.

Key Words: Ion exchanger, Lithium chloride, $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$, Separation.

INTRODUCTION

Salt lake resources are abundant in China and the lithium in the brine is very famous in the world¹. But now the exploitation of salt lake resources in China is just at the elementary and single-use level. At present, the demands for lithium chloride, especially the high pure lithium chloride, are increasing rapidly. 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 necessary to provide the raw material as pure as possible. The presence of small quantities of sodium in the lithium metal will make it highly reactive and much different in properties than pure 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, 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, antimonic and polyantimonic acid have been studied in the field, but it failed to practice because of the high cost. At present, to meet the rapidly increasing demand on lithium chloride, especially the high grade pure lithium chloride, it is urgent to remove Na^+ to produce of the high grade pure lithium chloride.

$\text{LiZr}_2(\text{PO}_4)_3$ possesses the NASICON-type (sodium super ion conductor) structure, composed of both MO_6 octahedra and PO_4 tetrahedra which are linked by their corners to form a three-dimensional (3D) network structure. The resulted

structure consists of type I and type II sites for the mobile Li ions to occupy. In $\text{LiZr}_2(\text{PO}_4)_3$, the Li^+ occupy type I sites (octahedral O-coordination) and in $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$ which also possesses the NASICON-type structure with a partial substitution $\text{Zr}^{4+} \rightarrow \text{La}^{3+} + \text{Li}^+$, the x Li ions occupy the type II sites (10-fold O-coordination). The occupation of Li ions at the type II sites is favorable for the chemical stability of materials^{2,3}.

The results showed that $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$ (LLZP) show higher exchange capacity towards Na^+ . The exchange capacity of LLZP was 41.3 mg/g. Compared with other methods, the novel Na specific ion exchanger of LLZP described here is a simpler and more convenient way to remove Na^+ from LiCl solution which suggest the promising application.

EXPERIMENTAL

All the chemicals *viz.*, Li_2CO_3 , ZrO_2 , La_2O_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ used in the experiment are of analytical grade.

General procedure: 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 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 Shimadzu TA-60 with the heating temperature from 20-900 °C at 20 °C/min in N_2 . XRD (X-Ray power diffraction) patterns for the sample was measured by Rigaku D/max-3B X-ray

diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). The Fourier transform infrared (FTIR) spectrum was recorded on a Thermo Nicolet Nexus in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$. The morphology of the sample was observed by JEOL JSM-5600LV SEM (scanning electron microscope).

Test of ion exchange properties: 1 g diffraction patterns of LLZP samples were added to 200 g of LiCl solution containing 0.06 % Na^+ . The concentration of Na^+ in solution is measured after stirring the solution for different time. The ion exchange capacity of LLZP sample was carried out at different temperature.

RESULTS AND DISCUSSION

Fig. 1 shows TG/DTA curve of the raw material. There are four endothermic peaks at 121, 204, 310 and 341 °C in TG/DTA curves. TG curve revealed the mass loss of 24.95 % which occurred at 20–600 °C, while no change in weight was found from 600–1000 °C. The following reaction can be expected to have mass loss of 24.72 %:

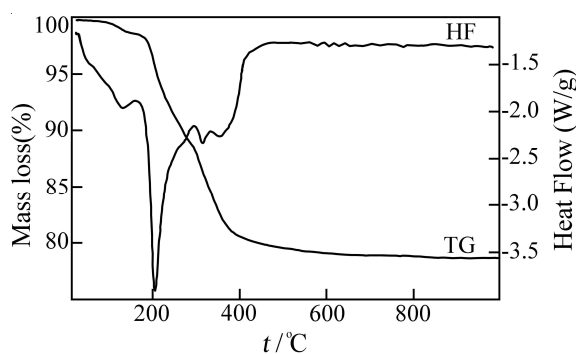
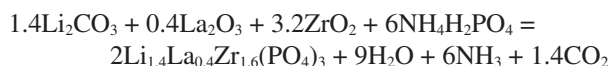


Fig. 1. TG/DTA curves of the raw material

The phase evolution of diffraction patterns LLZP was 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. It showed that La^{3+} did not affect the structure of the material. The LLZP structure was indexed in the rhombohedral system with lattice: rhomb-centered, space group and the cell parameters: $a = 0.88077 \text{ nm}$, $b = 0.88077 \text{ nm}$, $c = 2.2715 \text{ nm}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$.

Infrared absorption spectrum of LLZP is presented in Fig. 3. There are four kinds of basic vibration modes in PO_4^{3-} : $\nu_1(\text{A}_1)$, $\nu_2(\text{E})$, $\nu_3(\text{F}_2)$, $\nu_4(\text{F}_2)$, corresponding to the PO symmetric stretching vibration, PO_2 symmetric bending vibration, PO antisymmetric stretching vibration and PO_2 antisymmetric bending vibration. But, because of the influence of local point of symmetry and metal-oxygen groups in the crystal structure, the vibration of the PO_4^{3-} will change⁴⁻⁶. The spectra are dominated by intense, overlapping intramolecular PO_4^{3-} stretching modes that range from $1300\text{--}700 \text{ cm}^{-1}$. The frequency of the broad features between 700 and 850 cm^{-1} in the spectrum of LLZP are somewhat lower than expected for PO_4^{3-} stretching modes. In fact, bands in this region of the spectrum are often due to condensed phosphate groups such as $\text{P}_2\text{O}_7^{4-}$ or extended polyphosphate structures. However, there are no bands near

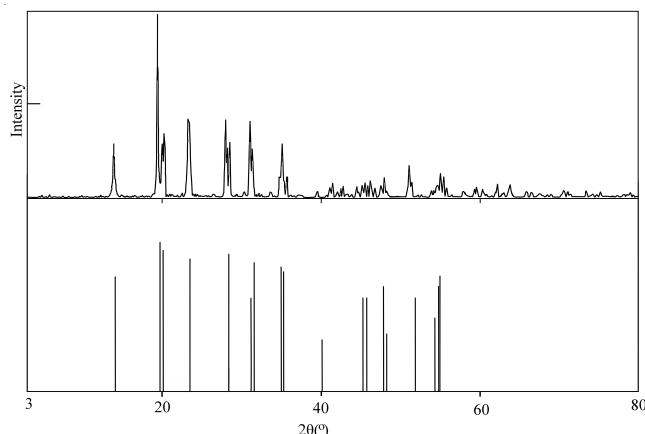


Fig. 2. XRD pattern of LLZP

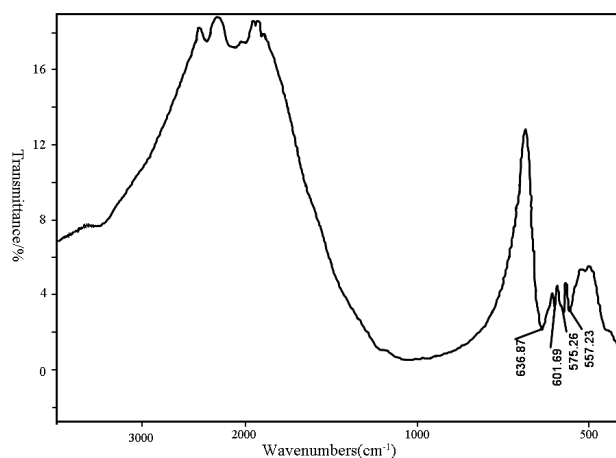


Fig. 3. FTIR spectrum of LLZP

750 cm^{-1} in the infrared spectrum to indicate the presence of bridging P-O-P groups. Two bands detected at 636 and 575 cm^{-1} of LLZP are assigned to ν_4 . The other two bands appears at 601 and 557 cm^{-1} in LLZP, which might be due to a small degree of disordering in the PO_4^{3-} anions as lanthanum is inserted in the compound.

Fig. 4 showed microstructure of the specimen pellet. It was seen that the specimen is highly dispersive particles with diameters ranged at $10\text{--}30 \mu\text{m}$.

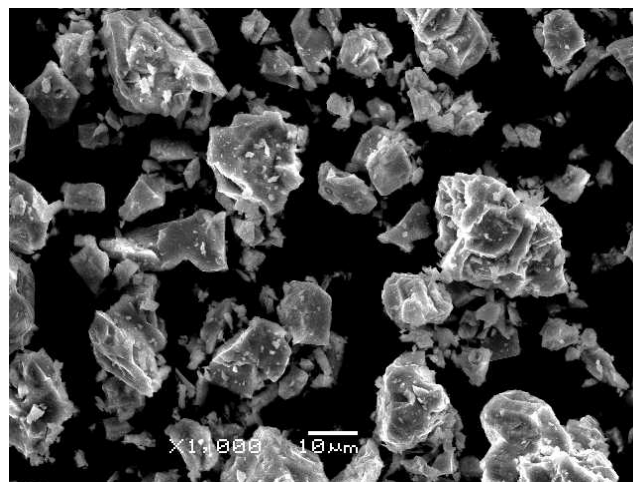


Fig. 4. SEM image of LLZP

Ion exchange properties: As shown in Fig. 5 the amount of Na⁺ exchange capacity increases with contact time and attains equilibrium within 200 min for ion exchanger at 20, 40, 60 and 80 °C. The higher temperature is good for ion exchange. The diffuse rate of Li⁺ and Na⁺ increases in LiCl solution, which accelerates Na/Li ion exchange on LLZP.

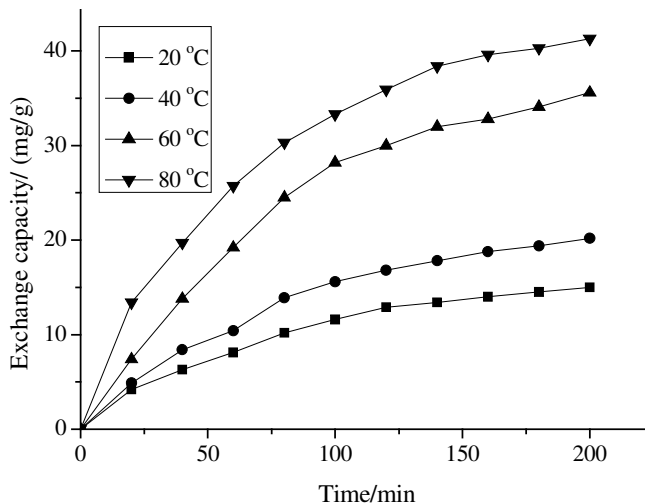


Fig. 5. Influence of time on exchange capacity

Kinetics law of Na/Li ion exchange fraction on LLZP depended on time can be express using JMAK equation⁶.

$$x = 1 - e^{-kt^n} \tag{1}$$

where x, ion exchange fraction of Na/Li on LLZP at t time; K, empirical parameter which is affected by temperature and granularity; n, time gene.

The equation may be linearized by taking the logarithm of both sides of eqn. 1 and linear form of JMAK equation can be given as eqn. 2:

$$\ln[-\ln(1-x)] = n \ln t + \ln K \tag{2}$$

The constant values of the isotherms were obtained from the slope and intercept of the plots (Fig. 6). The JMAK equation represents adequately the kinetics law of Na⁺ on LLZP.

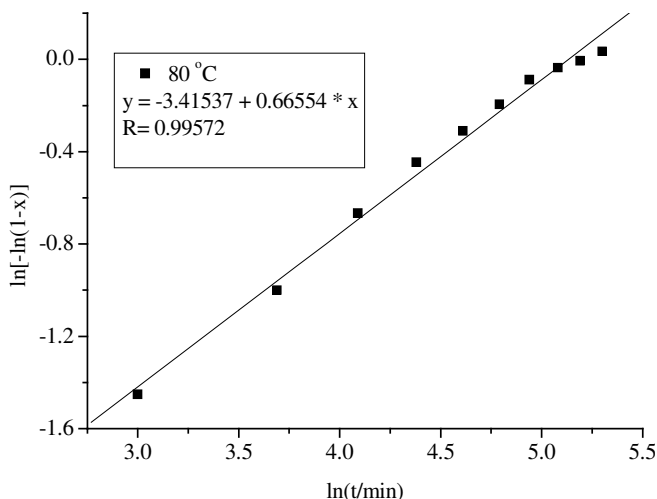
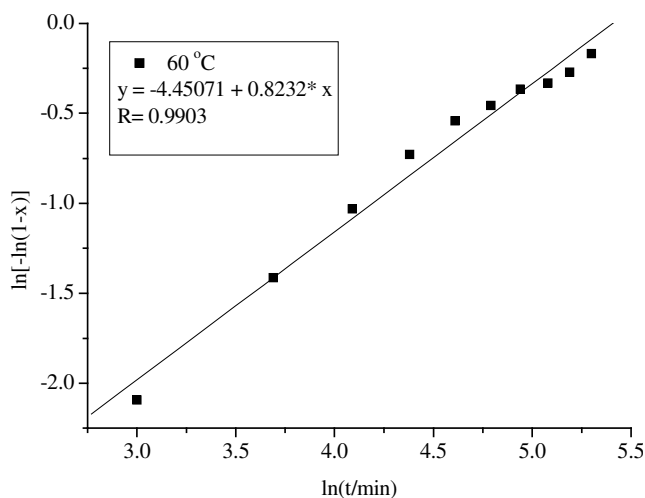
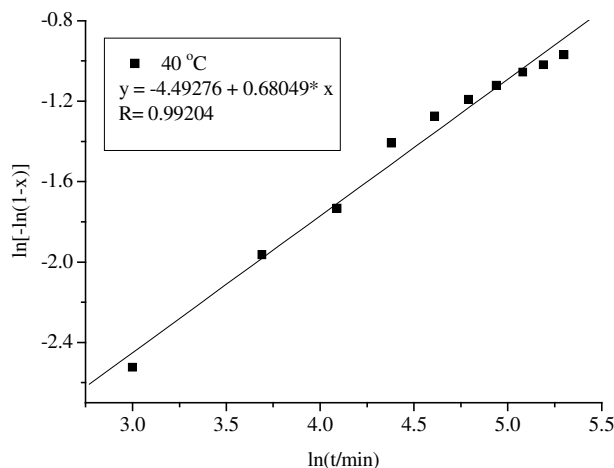
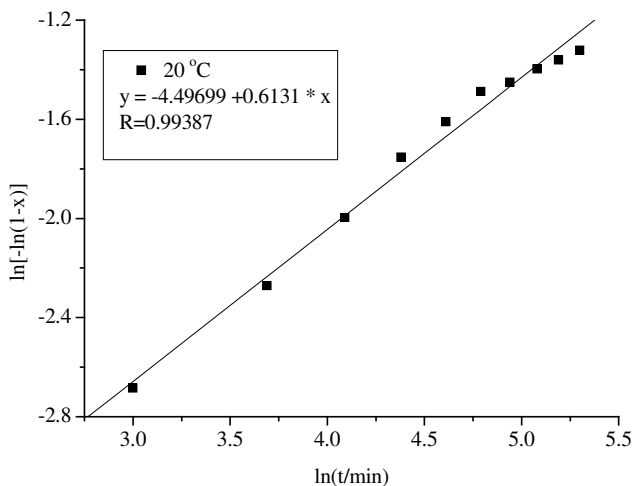


Fig. 6. $\ln[-\ln(1-x)]$ against $\ln t$ of Na/Li ion-exchange of LLZP

Conclusion

In this study, a novel sodium specific kind of ion exchanger $\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$ has been successfully prepared. The results of exchanging test showed that its exchange capacity reaches 41.3 mg/g, under 200 min at 80 °C. The JMAK equation represents adequately the kinetics law of Na⁺ on

$\text{Li}_{1.4}\text{La}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$. This method was a simpler and more convenient way to remove Na^+ from lithium chloride solution.

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