



Improved performance of Al-doped LiMn_2O_4 ion-sieves for Li^+ adsorption

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ABSTRACT

Al-doped $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ion-sieves were optimally synthesized with improved structural stability for Li^+ adsorption through hydrothermal synthesis method. Firstly, several parameters including the Al^{3+} doping content x , hydrothermal temperature, hydrothermal treatment time and calcination temperature were investigated to optimize the synthesis of $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ion-sieves for selecting unique spinel structure with low dissolution loss (R) for Li^+ adsorption. Then, the pristine LiMn_2O_4 (LMO) and optimized $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ (LAMO) ion-sieves were comparatively investigated from their microstructure and chemical state to Li^+ adsorption performance. The desorption ratio of Li^+ , adsorption capacity (Q) and the dissolution losses ($R_{\text{Mn}^{2+}}$ and $R_{\text{Al}^{3+}}$) of the ion-sieves were evaluated by adsorption-desorption experiments. It was found that the maximum equilibrium adsorption capacity Q_{LAMO} was 27.66 mg g^{-1} and the desorption ratio of Li^+ could reach 81.2% after 120 min. Meanwhile, $R_{\text{Mn}^{2+}}$ and $R_{\text{Al}^{3+}}$ of LAMO ion-sieve were very low in the desorption process. Moreover, LAMO ion-sieve also shows excellent stability and repeatability that the LAMO could still maintain a high adsorption capacity (19.5 mg g^{-1}) with very low $R_{\text{Mn}^{2+}}$ (3.71%) and negligible $R_{\text{Al}^{3+}}$ after repeating 5 times adsorption-desorption operation.

1. Introduction

Lithium is the lightest element in nature and extraction of lithium from Li-containing ores and salt lakes is of great importance for the wide range of its applications such as ceramics, pharmaceuticals, rechargeable batteries and other related fields [1–3]. China is abundant in lithium reserves where 13% of the world's lithium resources existed. However, about 85% of lithium resources are stored in salt lakes existing as brine lithium. With the increasing demand of lithium usage, especially lithium-ion batteries for electronic products and electric vehicles [4,5], thus, the technologies to achieve the extraction and recovery of lithium in salt lakes is keen to be developed.

In recent years, more and more researchers have paid their attention to the direction of lithium extraction. Up to date, approaches including but not limited to solvent extraction, chemical precipitation and lithium ion-sieves adsorption have been extensively attempted. Among them, solvent extraction is less used one due to its high cost and the high toxicity of organic solvents. Chemical precipitation is used more frequently, but it is only used for high capacity of Li^+ or low ratio of Mg/Li of brine [6]. Because of the high selectivity, structural stability, low cost and good adsorption performance, lithium ion-sieves adsorption has been considered as a promising lithium extraction method [7,8]. Spinel-type lithium manganese oxides with various Li/Mn molar ratios

such as $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ [9–13], $\text{Li}_4\text{Mn}_5\text{O}_{12}$ [14–18] and LiMn_2O_4 [19,20], have been widely studied as adsorbents for Li^+ recovery. Among these Li ion-sieves, LiMn_2O_4 shows relatively excellent selectivity and capacity in the adsorption of Li^+ combined with the use of acid. However, the real Li^+ adsorption capacity of LiMn_2O_4 is less than its theoretical adsorption capacity. This is due to the fact that the average valence of Mn in LiMn_2O_4 is +3.5 resulting in the Jahn-Teller effect [21] that the dissolution loss of Mn^{2+} in the desorption process is severe [22,23]. In order to overcome these drawbacks, various methods such as volumetric doping and surface modification for LiMn_2O_4 have been developed which are effective in reducing the dissolution loss of Mn^{2+} and improving cycling ability. For the dopants, some of the inert metal cations (M), such as Co, Cd, Ni, Mg, Li, Zn, can form M-O bond with O, and its bond energy is larger than that of Mn-O bond, which can improve the structural stability. Besides, these doping metals can increase the average valence state of Mn, decrease the content of Mn^{3+} , suppress the Jahn-Teller effect and reduce the dissolution loss of Mn^{2+} . Al has good potential for doping in addition to above-mentioned dopants owing to its low weight and structural stability. Moreover, the radius of Al^{3+} (0.57 Å) is very close to that of Mn^{3+} (0.66 Å) and the bond energy of Al-O bond is larger than that of Mn-O bond [24]. Hence, some efforts have been made for synthesis of Al-doped spinel-type lithium manganese oxides. Sun et al. [25] successfully synthesized

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$\text{Li}_{1.03}\text{Al}_{0.2}\text{Mn}_{1.8}\text{O}_{3.96}\text{S}_{0.04}$ ion-sieve by using sol-gel method and based upon template method. Li et al. [26] used polymethyl methacrylate (PMMA) as the template and prepared a porous $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ (P-LAMO) ion-sieve. In addition, Yu et al. [27] grinded stoichiometric LiCO_3 , MnO_2 and Al_2O_3 to prepare $\text{Li}_{1+x}\text{Mn}_{2-x-y}\text{Al}_y\text{O}_4$ with high-temperature solid-state method. The success in the preparation of $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ by different methods indicates that Al^{3+} can be embedded into the framework of LiMn_2O_4 under certain conditions. Therefore, the $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ composite ion-sieve with a high adsorption capacity and low dissolution loss could be concerned. Furthermore, an efficient and environmental friendly synthesis of $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ composite ion-sieves is required for the Li^+ adsorption.

In this study, a series of Al-doped LiMn_2O_4 ion-sieves were prepared by hydrothermal synthesis method using $\text{LiOH}\cdot\text{H}_2\text{O}$ as lithium source, co-precipitated with $\text{Mn}(\text{NO}_3)_2$ and $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$. We first optimized several parameters in the procedure of synthesizing $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ion-sieves to determine the best $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ion-sieve for Li^+ adsorption, including the Al^{3+} doping content x , hydrothermal temperature, hydrothermal treatment time and calcination temperature. Then the pristine LiMn_2O_4 and the optimal ion-sieves were further studied and their microstructure and stability in Li^+ adsorption process were comparatively investigated. Importantly, the structural stability of as-prepared ion-sieves were significantly improved, which make the spinel-typed ion-sieves promising for Li^+ recovery from salt lake.

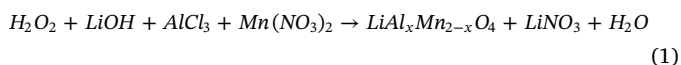
2. Experimental

2.1. Materials

The manganese nitrate (50% solution), aluminum chloride hexahydrate, lithium hydroxide monohydrate, hydrogen peroxide (30%) and ammonia hydroxide were purchased from the Sinopharm Chemical Reagent Co., Ltd. All of these chemicals are used in analytical grade without further purification.

2.2. Synthesis and characterization of $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ composite ion-sieves

Fig. 1 schematically illustrates the procedure of synthesis of $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ion-sieves. The reaction occurred, as shown in eq. (1):



$\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ion-sieve was synthesized with H_2O_2 as oxidant, LiOH

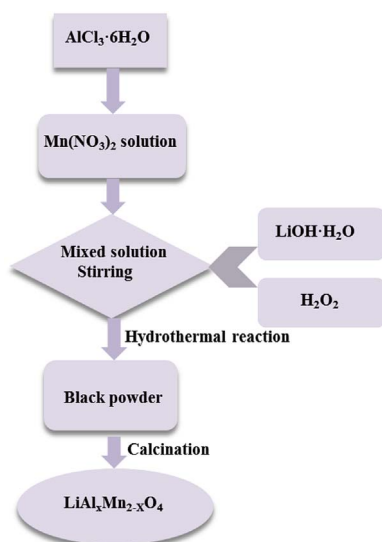


Fig. 1. Illustration of the synthetic route of LAMO ion-sieves.

Table 1
The synthetic details of LMO and LAMO ion-sieves.

Name	x	LiOH·H ₂ O (g)	Mn (NO ₃) ₂ solution (g)	AlCl ₃ ·6H ₂ O (g)	H ₂ O ₂ (mL)
LMO	0	2.31	6.44	0	1.5
LAMO	0.1	2.31	6.12	0.22	1.5

as lithium resource, co-precipitation of AlCl_3 and $\text{Mn}(\text{NO}_3)_2$ as aluminum resource and manganese resource.

The optimization of synthesis and characterization of $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ion-sieves could be found in supporting information. Several parameters including the Al^{3+} doping content x , hydrothermal temperature, hydrothermal treatment time and calcination temperature were systematically investigated to optimize the spinel structure and dissolution loss of $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ion-sieves for further Li^+ adsorption application. It is found the as-prepared $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ (LAMO) ion-sieve shows the best performance for Li^+ adsorption.

Briefly, 0.4 M $\text{Mn}(\text{NO}_3)_2$ and $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ in a molar ratio of $n(\text{Mn}^{2+}:\text{Al}^{3+}) = 1.9:0.1$ were dissolved in deionized water under continuously stirring, then the solution of $\text{LiOH}\cdot\text{H}_2\text{O}$ (1.1M) in a molar ratio of $n(\text{Li}^+:\text{Mn}^{2+}) = 3:1$ and 30% H_2O_2 were slowly dropped into the mixed solution simultaneously within 15 min, which was shown in Table 1. After that, the reaction was lasted for 180 min and then the suspension was transferred to the autoclave for hydrothermal reaction at 170 °C for 10 h. Subsequently, the resulted black product was filtered, washed and dried at 100 °C for 6 h. The black powder was finally calcined at 700 °C for 10 h to obtain LAMO ion-sieve in a tube furnace. As a control experiment, the pristine LiMn_2O_4 (LMO) ion-sieve was prepared via the similar procedure without Al doping.

The spinel structure of the LMO and LAMO ion-sieves were analyzed by X-ray diffraction (XRD, D8-ADVANCED, Germany BRUKER), which was carried out with a Rigaku diffractometer using $\text{Cu K}\alpha$ radiation. The lattice constants of above samples were fitted through Jade software. The morphological characteristics of samples were analyzed by scanning electron microscope (SEM, ITACHI-4800) and High Resolution Transmission Electron Microscope (HRTEM, JEOL-2100F). An X-ray photoelectron spectroscopy (XPS, Thermo Fisher, ESCALAB 250xi) was used to confirm the chemical state of the as-prepared LMO and LAMO ion-sieves.

For determining the chemical formula of LMO and LAMO ion-sieves, 0.1 g LMO and LAMO samples were first added to the mixture solution of 0.5 M HCl and H_2O_2 under continuously stirring, respectively. The supernatants were collected after dissolution completely, and then they were filtered using a syringe filter with a pore size of 0.2 μm . The obtained filtrates were used for analysis. Table 2 lists the actual chemical formula of LMO and LAMO which were determined by inductive coupled plasma optical emission spectrometer (ICP-OES, Optima7000DV, Perkin Elmer, USA).

2.3. Adsorption stability of LMO and LAMO ion-sieves

2.3.1. Dissolution loss R of Mn^{2+} and Al^{3+} in LAMO ion-sieves

Typically, LAMO ion-sieves were delithiated by adding 0.5 g powders into a 500 mL of HCl solution (0.1 M) under continuously stirring.

Table 2
The actual chemical formula of LMO and LAMO ion-sieves.

Name	Metal ion concentration (mg·L ⁻¹)			Molar ratio Li:Al:Mn	Formula
	Li ⁺	Al ³⁺	Mn ²⁺		
LMO	16.05	/	253.7	2.293:4.613(Li:Mn)	$\text{LiMn}_{2.01}\text{O}_4$
LAMO	12.01	4.908	179.5	1.716:0.182:3.265	$\text{LiAl}_{0.106}\text{Mn}_{1.902}\text{O}_4$

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