

Li⁺ extraction/adsorption properties of Li-Sb-Mn composite oxides in aqueous medium

MA Li-wen, CHEN Bai-zhen, SHI Xi-chang, ZHANG Kun

School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China

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Abstract: Series Li-Sb-Mn composite oxides with different Sb/Mn molar ratios were obtained by solid state reaction. Their structure, morphology and Li⁺ extraction/adsorption properties were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and atomic absorption spectrophotometry (AAS), respectively. XRD and SEM analyses reveal that the crystal of the products transfers from spinel to orthorhombic phase with the increase of molar ratio of Sb to Mn from 0.05 to 1.00. The Li⁺ extraction and adsorption experiments for these Li-Sb-Mn composite oxides demonstrate that the composite oxides can all be used as lithium inorganic adsorbents. The acid treated spinel Li-Sb-Mn composite oxide with Sb/Mn molar ratio of 0.05 has a high Li⁺ adsorption capacity of 33.23 mg/g in lithium solution. The Sb/Mn molar ratio of these Li-Sb-Mn composite oxides should be a crucial factor in determining their structure and Li⁺ extraction and adsorption properties.

Key words: Li-Sb-Mn composite oxides; lithium; extraction; adsorption

1 Introduction

Interest in lithium sources has been increasing because of its wide applications in rechargeable lithium batteries and other related fields. But the present lithium mineral reserves in the world cannot meet the requirement of lithium in the next two decades [1]. Therefore, to develop the proper technology to recover lithium from liquid lithium resource is of great value. Owing to their noticeable properties such as low toxicity, low cost, high chemical stability and high Li⁺ adsorption capacity, inorganic lithium adsorbents are suggested to be promising to recover lithium from liquid lithium resource of sea water, geothermal water, salt lake brine and so on [2–3]. LiSbO₃ was found to have Li⁺ extraction and adsorption property in the early years [4–5]. After acid treatment Li⁺ adsorption capacity of LiSbO₃ is about 17 mg/g [6]. Recently, spinel type LiMn₂O₄ was studied extensively as a typical inorganic lithium adsorbent precursor. After topotactic extraction of Li⁺ from LiMn₂O₄, it shows Li⁺ adsorption property with the capacity of around 20 mg/g [7–8]. But during acid treatment Mn³⁺ in LiMn₂O₄ will be disproportionate to Mn⁴⁺ and Mn²⁺. Mn⁴⁺ remains in the spinel skeleton

and Mn²⁺ dissolves in solution to destroy the spinel structure gradually [9–10]. To overcome this shortage, some researchers have tried to replace parts of Mn with different cations such as Ni²⁺, Mg²⁺, Al³⁺, Cu²⁺ and Co³⁺ into LiMn₂O₄ to enhance its structural stability [11–14]. Most of these cations have positive effects, but Sb was rarely reported to be a substituent element. Therefore, changing the molar ratio of Sb/Mn to synthesize Li-Sb-Mn composite oxides may be able to find the materials more advanced than LiSbO₃ and LiMn₂O₄ for lithium inorganic adsorbents. In the present work, series Li-Sb-Mn composite oxides were synthesized by simple solid state reaction.

2 Experimental

2.1 Synthesis of materials

Various Li-Sb-Mn composite oxides were prepared by heating mixtures of Li₂CO₃, MnO₂ and Sb₂O₃ with different Li/Mn/Sb mole ratios in air at 800 °C for 12 h. The Sb/Mn molar ratio of these Li-Sb-Mn composite oxides varied from 0.05 to 1.00, but Li/(Sb+Mn) molar ratios were fixed at 0.5. According to the molar ratio of Sb/Mn they were noted as S-0.05, S-0.33 and S-1.00, respectively. For comparison, pure LiMn₂O₄ and pure

LiSbO₃ were also synthesized by the same method. And they were designated as S-0 and S-∞ because they can be regarded as special Li-Sb-Mn composite oxides with Sb/Mn molar ratio of zero and infinity.

2.2 Li⁺ extraction/adsorption experiment

A constant mass (0.100 g) of Li-Sb-Mn composite oxides were immersed in 100 mL HCl solution (0.5 mol/L) at 25 °C, respectively. The concentrations of lithium, manganese and antimony ions in the solution after attainment of equilibrium were determined by an atomic absorption spectrophotometer (TAS-999F, Beijing). The test methods of Li, Mn and Sb were referred to standards for mining industry of DZ/T 0064.30—93 and DZ/T 0064.32—93 and national standard of GB/T 1819. 6—2004. All the metallic element extraction ratios were calculated by the following equation:

$$R = \frac{m}{m_0} \times 100\% \quad (1)$$

where R is the extraction ratio of metallic element; m is the mass of metallic element in the solution; m_0 is the mass of element in the original material.

After the above acid treatment the samples S-0, S-0.05, S-0.33, S-1 and S-∞ were denoted as H-0, H-0.05, H-0.33, H-1 and H-∞, respectively. A constant mass (0.100 g) of the acid-treated samples were immersed in 50 mL mixed solution (LiCl+LiOH) at 25 °C for 24 h. Li⁺ concentration of the initial mixed solution was 0.05 mol/L and the pH value was fixed at 12. After attainment of equilibrium the lithium concentration in the solution was determined by an atomic absorption spectrophotometer. The lithium adsorption capacities of these acid-treated samples were calculated by mass balance relation as the following equation:

$$Q_e = \frac{(\rho_0 - \rho_e)V}{m_1} \quad (2)$$

where Q_e is the lithium adsorption capacity; ρ_0 and ρ_e are the initial and equilibrium lithium ion concentrations in the solution, respectively; V is the solution volume; and m_1 is the mass of acid-treated sample.

2.3 Characterization

The powder XRD patterns of these Li-Sb-Mn composite oxides and their acid-treated forms were obtained on a Rigaku X-ray diffractometer (D/max 2550) equipped with a Cu anticathode (Cu K_α radiation $\lambda = 0.154\ 056$ nm) at room temperature. The measurements were recorded under Bragg-Brentano geometry at 2θ with step of 10 (°)/min in the range of 10°–80°. The particle morphology of Li-Sb-Mn composite oxides was examined with a scanning electron microscope (SEM, Sirion200).

3 Results and discussion

3.1 Structure and morphology of Li-Sb-Mn composite oxides

Figure 1 shows the XRD patterns of Li-Sb-Mn composite oxides. The reflections of sample S-0 can be indexed to pure spinel-type LiMn₂O₄ whose characteristic peaks are marked by triangle symbols. LiMn₂O₄ is a typical spinel lithium manganese oxide with Li at the 8a tetrahedral sites and Mn (III), Mn (IV) at the 16d octahedral sites of a cubic closed-packed oxygen framework [15], as demonstrated in Fig. 2(a). Similar to sample S-0, pure LiSbO₃ is obtained for sample S-∞ and its characteristic peaks are marked by diamond symbols. This perovskite type oxide has an orthorhombic crystal structure with an array of hexagonally closed packed oxygen atoms in which the cations occupy two-third of the octahedral sites, as shown in Fig. 2(b) [16]. Both LiMn₂O₄ and LiSbO₃ have three dimensional tunnels for Li⁺ extraction and reinsertion.

For sample S-0.05 almost all the reflections can be readily indexed to cubic phase of LiMn₂O₄, which means that Sb is incorporated into the spinel lattice. Thus sample S-0.05 can be regarded as Sb-substituted spinel. The XRD diffraction peaks of sample S-0.05 move to lower angle direction with the increase of lattice parameter a from 0.823 52 to 0.827 31 nm compared with the pure LiMn₂O₄. The increase of the lattice parameter is caused by the incorporation of Sb⁵⁺. Sb⁵⁺ substituting parts Mn⁴⁺ can enhance the content of Mn³⁺ to keep the charge balance, and the average Mn—O bond length of Mn³⁺ (0.201 nm) is larger than that of Mn⁴⁺ (0.191 nm) [17]. This cell expansion means a decrease of the force between atoms in the structure.

The reflections of sample S-0.33 can be indexed to both LiMn₂O₄ and LiSbO₃. The emergence of LiSbO₃ indicates that Sb is not fully integrated into the spinel

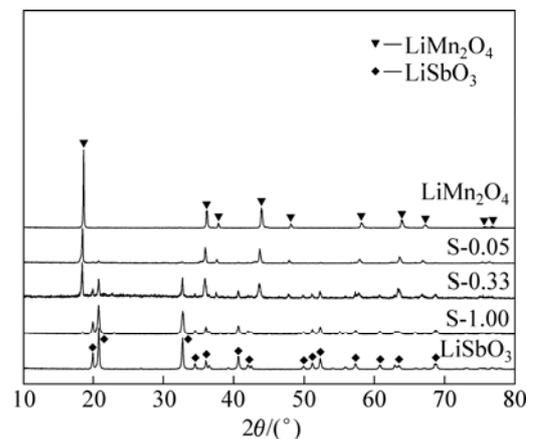


Fig. 1 XRD patterns of Li-Sb-Mn composite oxides

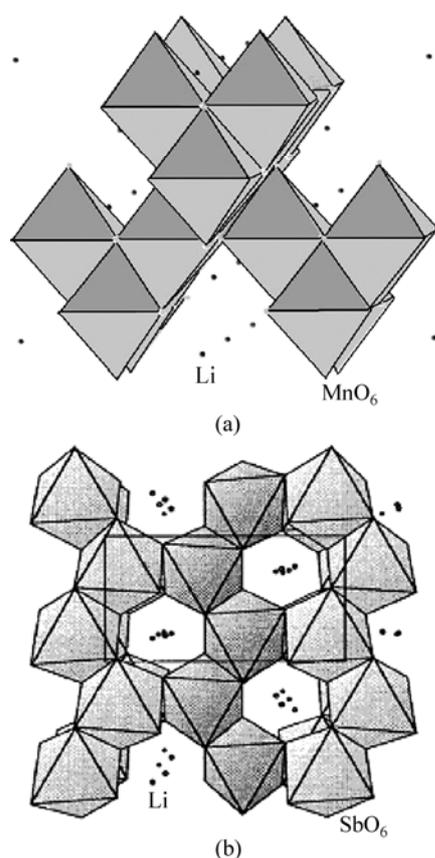


Fig. 2 Schematic representation of structure of LiMn_2O_4 (a) and LiSbO_3 (b) [16]

lattice when the added Sb is excessive. In this case, the “real” Sb content in the spinel lattice is lower than the corresponding theoretical value. Therefore, sample S-0.33 is not of a pure phase, but a mixture in which antimony and manganese ions diffuse into spinel and perovskite mutually to form complex solid solutions.

Sample S-1.00 shows the single phase of LiSbO_3 . The spinel phase of LiMn_2O_4 almost disappears. It is reasonable to consider that if molar ratio of Sb to Mn is high enough, LiSbO_3 will become the majority and Mn will be incorporated into the LiSbO_3 structure as substituent element. Because of the incorporation of Mn into the LiSbO_3 structure, a cell contraction occurs with the XRD diffraction peaks of S-1.00 shifting to higher angle direction when compared with those of LiSbO_3 .

Figures 3(a), (b) and (c) show the SEM images of samples S-0.05, S-0.33 and S-1.00, respectively. Sample S-0.05 shows the typical spinel morphology of LiMn_2O_4 with small and uniform octahedral crystals, while sample S-1.00 presents sheet structure as LiSbO_3 . The morphology difference between samples S-0.05 and S-1.00 indicates these two Li-Sb-Mn composite oxides are classified, as explained by XRD analysis, into two categories: Sb-substituted spinel and Mn-substituted perovskite. The sample S-0.33 presents uneven grains

involving large octahedra and small polyhedra. The microstructure of sample S-0.33 can be regarded as a combination of both LiMn_2O_4 and LiSbO_3 , and the spinel type morphology seems to be the primary one.

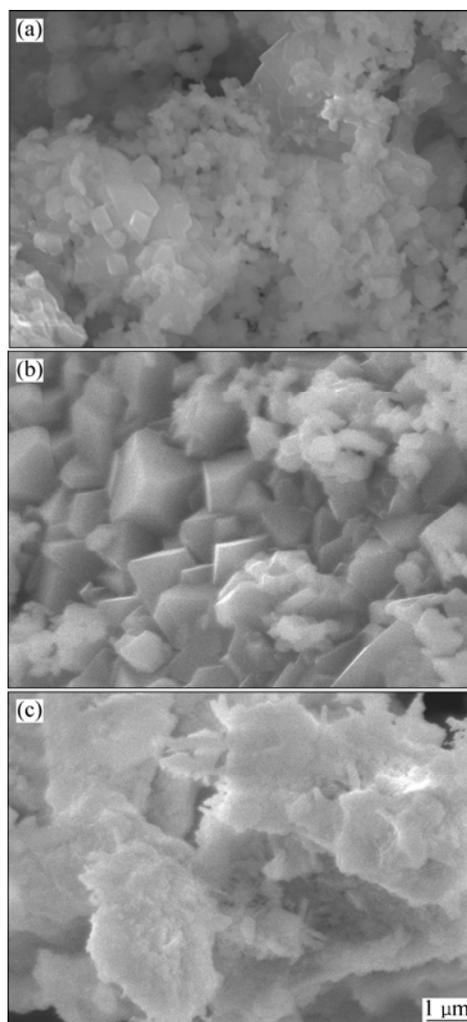


Fig. 3 SEM images of Li-Sb-Mn composite oxides: (a) S-0.05; (b) S-0.33; (c) S-1.00

3.2 Acid treatment of Li-Sb-Mn composite oxides

Samples S-0, S-0.05, S-0.33, S-1.00 and S-∞ were immersed in acid solution to investigate their extractabilities of lithium and other metallic elements. The extraction ratios of lithium, manganese and antimony were determined after the attainment of equilibrium. The results are shown in Table 1. 95.32% Li, 26.20% Mn and 29.34% Sb could be extracted from S-0.05, which are higher than those from S-0 (LiMn_2O_4). Because the Mn dissolution results from a disproportionation reaction of Mn^{3+} ($\text{Mn}^{3+} \rightarrow 1/2\text{Mn}^{4+} + 1/2\text{Mn}^{2+}$) in the acid solution, the replacement of Mn by Sb^{5+} should increase the Mn^{3+} content in the spinel to keep the charge balance, thus would accelerate the dissolution of Mn. The cell expansion of S-0.05 which reduces the force between atoms in the structure

Table 1 Extraction ratios of metallic element of Li-Sb-Mn composite oxides

Extraction ratio %	$R(\text{Li})/\%$	$R(\text{Mn})/\%$	$R(\text{Sb})/\%$
S-0(LiMn_2O_4)	90.12	21.27	–
S-0.05	95.32	26.20	29.34
S-0.33	80.55	34.20	4.34
S-1.00	34.31	4.19	6.65
S- ∞ (LiSbO_3)	36.00	–	12.99

should be the main reason of the increase in Li and Sb extraction ratios.

The Li extraction ratio of S-1.00 is about 35%, similar to that of S- ∞ (LiSbO_3), but its Sb extraction ratio (6.65%) is only half of the value of S- ∞ . This may mean that the substituted Mn can restrict the dissolution of Sb, but not affect the extractability of Li. In addition, it is noticeable that the Mn extraction ratio of S-1.00 is much lower than that of S-0.05 or S-0 (LiMn_2O_4). This may imply a more stable structure for S-1.00 compared with S-0, S-0.05 and S- ∞ .

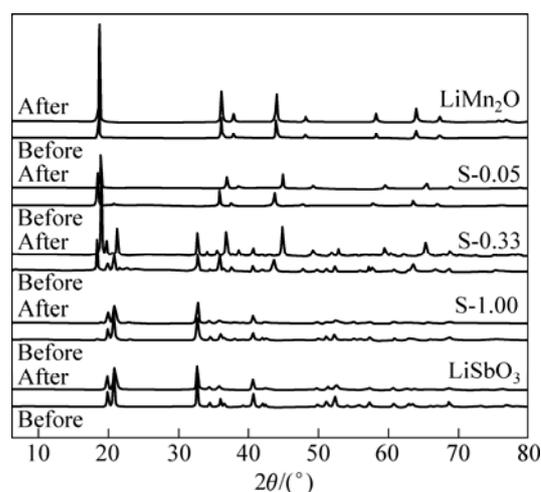
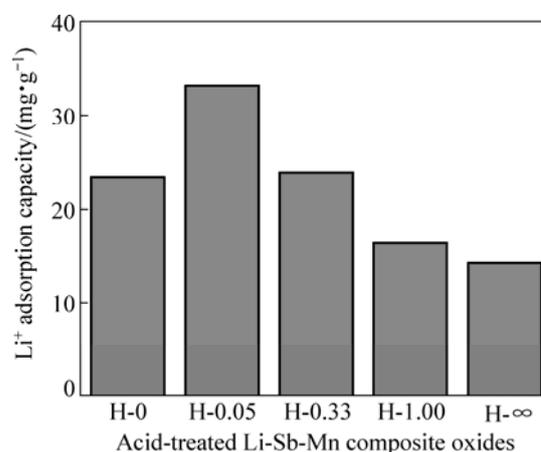
For sample S-0.33, its extractabilities of Li and Mn resemble those of S-0.05, while its Sb extractability is similar to that of S-1.00.

Because the lattice expansion or contraction has the same effect on the extraction of Li^+ and other metallic elements (Mn and Sb), it is difficult to decrease the dissolution of Mn and Sb while increase the extraction of Li^+ . However, only those materials with low Mn and Sb dissolution ratios and high Li^+ extraction ratio in the acid treatment can be transformed to the perfect lithium adsorbents, which is the target material to adsorb Li^+ during the subsequent experiments. So, to obtain excellent lithium adsorbent from Li-Sb-Mn composite oxides, further adjustments to the molar ratio of Sb to Mn and experimental conditions are needed in the future.

The XRD patterns of the Li-Sb-Mn composite oxides before and after acid treatment are presented in Fig. 4. The XRD patterns of all Li-Sb-Mn composite oxides after acid treatment are almost unchanged, only with the diffraction peaks shifting to higher angle direction. This indicates that the extraction of Li^+ out of Li-Sb-Mn composite oxides proceeds topotactically, maintaining the cubic or orthorhombic structures, but their lattices contract as a result of the $\text{Li}^+\text{-H}^+$ ion exchange reaction ($r_{\text{H}^+} < r_{\text{Li}^+}$).

3.3 Lithium adsorption property of acid-treated Li-Sb-Mn composite oxides

Acid-treated Li-Sb-Mn composite oxides (notated as H-0, H-0.05, H-0.33, H-1.00 and H- ∞) were immersed in mixed solution ($\text{LiCl}+\text{LiOH}$, $c_{\text{Li}^+}=0.05$ mol/L, $\text{pH}=12$) for the lithium adsorption study. The lithium adsorption results are shown in Fig. 5. The Li^+

**Fig. 4** XRD patterns of Li-Sb-Mn composite oxides before and after acid treatment**Fig. 5** Li^+ adsorption capacity of acid-treated Li-Sb-Mn composite oxides

adsorption capacity of sample H-0.05 is 33.23 mg/g, which is the highest among these acid-treated Li-Sb-Mn composite oxides. The Li^+ adsorption capacities of samples H-0.33 and H-1.00 decrease gradually with the increase of the Sb/Mn molar ratio. However, they are still higher than or close to those of H-0 (23.46 mg/g) and H- ∞ (14.15 mg/g). This means that Li-Sb-Mn composite oxides S-0.05, S-0.33 and S-1.00 have significant Li^+ adsorption capacities. The Li^+ adsorption property of S-0.05 and S-0.33 is better than that of pure LiMn_2O_4 and LiSbO_3 . They can all be used as lithium inorganic adsorbents. The effort to investigate these Li-Sb-Mn composite oxides more systematically is underway.

4 Conclusions

1) Series Li-Sb-Mn composite oxides were obtained by conventional solid state reaction. The crystal of the products transferred from spinel to orthorhombic phase

with the increase of the Sb/Mn molar ratio from 0.05 to 1.00. Sample S-0.05 is spinel with a cell expansion compared with LiMn_2O_4 due to the incorporation of Sb, while sample S-1.00 has orthorhombic structure with a cell contraction compared with LiSbO_3 because of the incorporation of Mn. Sample S-0.33 is an intergradation composed of both spinel and orthorhombic phases.

2) The Li-Sb-Mn composite oxides all show Li^+ extraction property in acidic solution. The Li^+ extractability is decreased with the increase of the Sb/Mn molar ratio. Due to the cell expansion, the Sb and Mn extraction ratios of sample S-0.05 are relatively high, which may suggest an unstable structure. However, sample S-1.00 exhibits relatively low Sb and Mn extraction ratios, which implies a more stable structure due to the cell contraction.

3) The acid-treated Li-Sb-Mn composite oxides all show Li^+ adsorption property in aqueous solution, making them advanced lithium inorganic adsorbents. In particular, sample H-0.05 shows a high Li^+ adsorption capacity of 33.23 mg/g in lithium solution.

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Li-Sb-Mn 复合氧化物在水溶液介质中的脱 Li^+ /吸 Li^+ 性能

马立文, 陈白珍, 石西昌, 张 坤

中南大学 冶金科学与工程学院, 长沙 410083

摘 要: 由固相法合成了不同 Sb/Mn 摩尔比的系列 Li-Sb-Mn 复合氧化物, 利用 X 射线衍射仪(XRD)、扫描电子显微镜 (SEM) 和原子吸收分光光度计 (AAS) 分别表征了其结构、形貌和锂离子脱出/吸附性能。XRD 和 SEM 分析表明, Li-Sb-Mn 复合氧化物随着 Sb/Mn 摩尔比从 0.05 提高到 1.00, 晶型由尖晶石型转变为正交相。 Li^+ 脱出/吸附实验表明, 不同 Sb/Mn 配比的复合氧化物都可以作为锂无机吸附剂。其中, 酸浸改型后的尖晶石锂镧锰复合氧化物($n(\text{Sb})/n(\text{Mn})=0.05$)在含锂溶液中具有较高的锂离子吸附容量, 达到 33.23 mg/g。Sb/Mn 摩尔比是决定该复合氧化物的结构和脱 Li^+ /吸 Li^+ 性能的主要因素。

关键词: 锂镧锰复合氧化物; 锂; 抽提; 吸附