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Preparation Method and Lithium Adsorption Property of λ-MnO_2-Silica Composite

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A new composite material based on λ-MnO_2 and macroporous silica was prepared by heat-treatment of the silica beads impregnated with a mixed aq. solution of lithium and manganese nitrates (Li/Mn molar ratio = 0.5), followed by acid-treatment. This composite can adsorb Li^+ ion selectively and has merit of usable for column operation.

λ-MnO_2[1] prepared by an acid-treatment of a spinel type manganese oxide ($LiMn_2O_4$) has high selective adsorbability for Li^+ ion, and is expected as one of promising adsorbent materials for the separation and concentration of Li^+ ion from seawater[2,3] or geothermal brine.[4] However, λ-MnO_2 is somewhat unsuitable for practical applications because it is formed as fine powder as well as many other inorganic ion-exchanger materials. For the purpose of making suitable particle size for column operation, Sagara et al., prepared a spherical composite material by dispersing microcrystalline λ-MnO_2 in macroporous cellulose-gel beads.[5] This method, however, has drawbacks as follows: (1) the size and uniformity of the gel beads are strongly dependent upon the producing conditions;[5] (2) the complexing with an organic materials gives rise to reduce the temperature and radiation resistance. In order to overcome these demerits, we proposed a new method for the preparation of suitable size of particle by producing composite materials made of microcrystalline inorganic ion-adsorbents and porous inorganic materials.[6] By this method, the inner wide space of open pores existed in the porous inorganic material is used as a solid-solid reaction field for producing the ion adsorbent.

In this paper, the preparation method and adsorbability for alkali metal ions on the composite of λ-MnO_2 and macroporous silica will be described.

The preparation procedure to obtain λ-MnO_2 crystallized in macropore of spherical silica beads (CMS) is as follows: 10 g of spherical macroporous silica beads[7] (SL) dried at 200 °C were added to 20 cm^3 of 6 M (1 M=1 mol dm^{-3}) mixed aq. solution of lithium- and manganese- nitrates (Li/Mn molar ratio=0.5) and kept under reduced pressure to impregnate the solution into SL for about 30 min. After the excess solution was aspirated out, the product was dried at 60 °C and 160 °C for each 12 h, and heated at 400, 600, 800, or 1000 ℃ for 4 h (PCMS). Then about 2 g of the samples were added to 400 cm^3 of 0.2 M HCl solution and the mixture was allowed to stand at room temperature for 4 days with occasional shaking to extract lithium. The acid solution was exchanged twice a day. The products were washed with water and dried at 60 ℃ (CMS).

The X-ray diffraction (XRD) patterns of SL and the composite samples were shown in Fig. 1. The XRD peak intensities of $LiMn_2O_4$ 111 in PCMSs varied with the heating temperature. Among the samples, PCMS-2 prepared by heating at 600 ℃ has the strongest intensity of the peak. Because amorphous silica transformed to α-quartz or tridymite so as to decrease its surface area and formation of Mn_2O_3 instead of $LiMn_2O_4$ at higher heating temperature above 800 ℃,

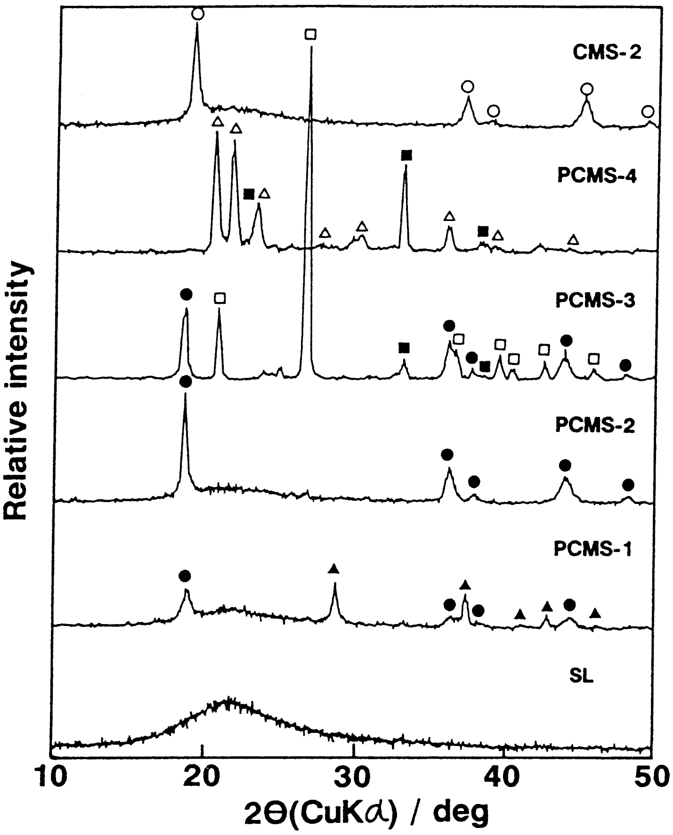


Fig. 1. X-Ray powder diffraction (XRD) patterns of SL and composite samples. The PCMS samples were prepared by heating at 1: 400°; 2: 600°; 3:800° and 4: 1000℃ for 4 h. CMS-2 was obtained by HCl-treating of PCMS-2, ●:$LiMn_2O_4$, ▲: MnO_2, ■:Mn_2O_3, □: α-quartz, △: tridymite, ○: λ-MnO_2.

Table 1. Chemical compositions and specific surface areas (SSA) of the samples

Sample	Li		Mn		Molar ratio	SSA
	wt%	mole	wt%	mole	Li/Mn	m^2g^{-1}
$LiMn_2O_4$ theoretical	3.84	0.553	60.77	1.106	0.500	-
$LiMn_2O_4$ prepared[a)]	3.63	0.523	60.52	1.102	0.475	2
λ-MnO_2 prepared[b)]	0.28	0.041	60.98	1.110	0.037	15
PCMS-1	1.15	0.165	19.91	0.362	0.456	10
PCMS-2	1.16	0.167	21.65	0.394	0.425	11
PCMS-3	0.96	0.139	16.01	0.291	0.477	6
PCMS-4	0.12	0.017	8.23	0.150	0.115	ND[c)]
CMS-2	0.09	0.013	17.64	0.321	0.039	16

SSA value of SL was 13 m^2 g^{-1}.

a) Obtained by heating materials, precipitated from mixed nitrates solution, at 600 ℃ for 4 h.

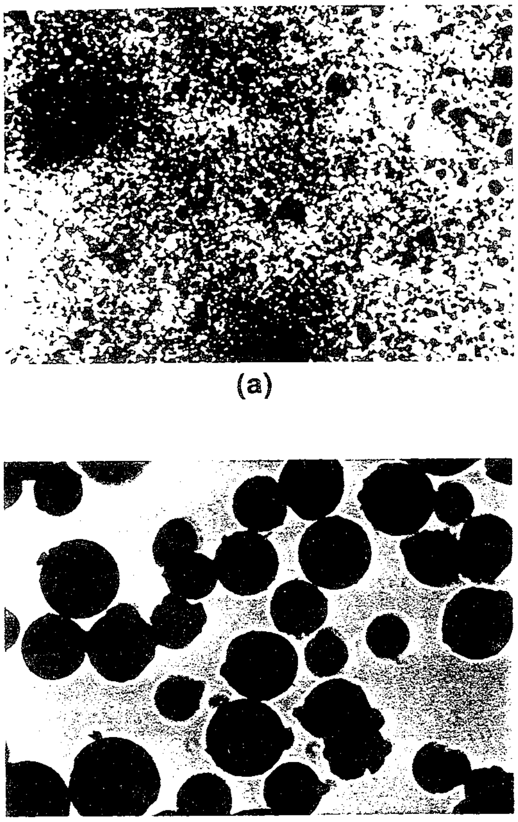
b) HCl-treated product of a).

c) Not detected.

Table 2. XRD data for PCMS-2 and CMS-2

h k l	$LiMn_2O_4$ (dÅ)		λ-MnO_2 (dÅ)	
	a)	PCMS-2	b)	CMS-2
1 1 1	4.72	4.77	4.64	4.65
3 1 1	2.47	2.48	2.42	2.42
2 2 2	2.37	2.38	2.31	2.33
4 0 0	2.05	2.06	2.01	2.01
3 3 1	1.88	1.89	1.84	1.85

a) ASTM 18-736.[8)]
b) Values reported by Hunter.[1)]


(a)

(b)

Fig. 2. Microscopic photograph of λ-MnO_2[a)] (a) and CMS-2 (b) (x100).
a) Sample is same as Table 1.

the composite of SL and $LiMn_2O_4$ became to be more difficult to form. CMS-2 obtained by the acid-treatment of PCMS-2 was a desired composite material consisted of λ-MnO_2 and SL. Table 1 shows the chemical compositions and specific surface area (SSA) of the samples. The metal contents of the samples were determined by atomic absorption spectrometry after the samples were dissolved in a mixed solution of concentrated HNO_3 and HCl. The SSAs were measured by N_2-BET single point method for the samples heated at 250 °C for 20 min. The Li/Mn molar ratios (0.43-0.48), calculated from chemical analyses of PCMS-1-PCMS-3, were somewhat lower than the ideal ratio (0.5) of $LiMn_2O_4$. But the XRD data for PCMS-2 and CMS-2 (Table 2) were in good agreement with the reported values for $LiMn_2O_4$[8)] and λ-MnO_2,[1)] respectively. The found SSA value of SL was 13 m^2 g^{-1}. The SSA decreased by complexing of $LiMn_2O_4$, and increased after acid-treating the composite because of formation of λ-MnO_2 having relatively high SSA. However, the SSAs of PCMS-3 and PCMS-4 prepared by heating above 800 °C decreased appreciably owing to destruction of the pore structure of SG and most of the manganese oxides was put inside the silica beads. Therefore unsoluble black materials still remained in these PCMSs after reaching with the mixed acid solution and, consequently, the apparent contents of lithium and manganese were fairly decreased. The amount of λ-MnO_2 hold in per g CMS calculated from the manganese content of CMS-2 was 0.28 g and almost the same as that of the wet cellulose-gel beads (0.32 g).[5)] The microscopic photograph of λ-MnO_2 samples and CSM-2 are shown in Fig. 2. Spherical composite materials with diameter of 0.05-0.2 mm are observed.

Adsorption data of alkali metal ions on the CMS from a mixed metal ions solution are shown in Table 3. Adsorption tests were carried out by the batch equilibration. The

Table 3. Adsorption data of alkali ions on λ-MnO_2 sample and CMS-2 from a mixed metal ions solution

Sample	Adsorption/%				
	Li^+	Na^+	K^+	Rb^+	Cs^+
λ-MnO_2[a)]	98.6	ND[b)]	ND	ND	ND
CMS-2	98.3	ND	ND	ND	ND

a) Sample is same as Table 1.
b) Noticeable changes of metal ions concentration before/after adsorption were not detected.

sample (0.02 g) was immersed in 10 cm^3 of the solution prepared by adding reagents (LiCl, NaCl, KCl, RbCl, CsCl) to give initial concentration of each metal of 1 x 10^{-3} M, to a 0.2 M trisaminomethane and 0.1 M HCl buffer solution of pH 8.5. The concentration of metal ions were determined by atomic absorption spectrometry. The amounts of lithium adsorbed were calculated from the concentrations in the solution subtracted from the initial concentrations. Only Li^+ ion was adsorbed on both samples. In spite of great difference of λ-MnO_2 amounts responsible for the adsorption in each sample, there was no difference of percent adsorption of Li^+ ion. It might be attributed to the low equilibrium concentration of Li^+ ion in the solution.

The amount of λ-MnO_2 hold in the SL is three or four-hold in contrast with a sintered glass filter[6)] which has macropores with diameter of 10-16 μm. These results seem to be suggesting that the amount of oxide(s) allowed to be hold in a composite prepared by our presented method is considerably dependent on the porous properties of an inorganic porous material used.

The preparation method presented here should be applicable to various combinations of inorganic ion-exchangers and porous inorganic materials.

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7) Total surface area: 10 m^2 g^{-1}, pore size (average): 3000 Å, bead size: 100-300 μm, pore volume: 1 cm^3 g^{-1}. Data from IBF catalog.

8) ASTM 18-736.

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