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Lithium Isotope Selectivity of Sorbents Prepared from Lithium Manganese Oxides

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ABSTRACT

Sorbents are prepared by extracting lithium ions from lithium manganese oxides with the lithium/manganese mole ratio (Li/Mn ratio) varying between 0.42 and 0.84, and their lithium isotope selectivities are investigated. All the sorbents are ^{6}Li-specific and the values of the ^{7}Li-to-^{6}Li isotopic separation factor (*S*) are between 1.0040 and 1.0092 at 25°C. The *S* value is slightly dependent on the Li/Mn ratio; it takes on the maximum at a Li/Mn ratio of 0.5 and decreases as the ratio deviates from this value. This indicates that the lithium isotope effect between the tetrahedral sorption sites of the sorbents and the external solution phase is larger than that between the octahedral sorption sites and the solution phase.

INTRODUCTION

Naturally occurring lithium consists of two stable isotopes (^{6}Li and ^{7}Li), and each of them has an important application in nuclear science and industry. The largest demand for isolated or enriched lithium isotopes in the future will be in deuterium–tritium fusion power reactors; lithium compounds rich in ^{6}Li

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will be required for the tritium breeder blanket:

$$^{6}\text{Li} + \text{n} \rightarrow \text{T} + {}^{4}\text{He}$$

Methods of separating lithium isotopes have been studied, and their applicability to large-scale enriched lithium isotope production has been assessed (1). Ion-exchange column chromatography is one of the promising methods. Commercially available organic ion exchangers are usually used as column packing material, and a single-stage separation factor of up to about 1.003 is observed at room temperature. This isotope separation effect is rather small compared to those in the amalgam and macrocyclic polyether systems (2, 3).

A way to realize large lithium isotope separation in ion-exchange chromatographic systems may be to develop new ion exchangers that exhibit large lithium isotope effects. In previous papers (4, 5) we reported that some inorganic sorbents and ion exchangers show much larger lithium isotope effects than organic ion exchangers. They include sorbents prepared from $MgMn_2O_4$ and Mg_2MnO_4.

The sorbent prepared from $LiMn_2O_4$ also exhibits large lithium isotope effects compared with organic ion exchangers (6). This sorbent retains the spinel-type structure the precursor possesses. It is known that lithium manganese oxide $Li_{1+x}Mn_{2-x}O_4$ has a spinel-type structure in the range of x from 0 to 0.33, or equivalently, when the mole ratio of lithium to manganese (Li/Mn ratio) is between 0.5 and 0.8 (7). The corresponding sorbents, MnO_2(Li), prepared by extraction of lithium ions retain the same structure. There are two kinds of lithium ion sorption sites in MnO_2(Li), i.e., octahedral and tetrahedral sites formed by six and four oxide ions, respectively. Ideally, MnO_2(Li) obtained from $LiMn_2O_4$ (one end member) has only tetrahedral sites. In this case the chemical formula of MnO_2(Li) can be expressed as $(\ )[Mn_2^{4+}]O_4$ where ( ) denotes the tetrahedral vacant site (8). The proportion of the octahedral site increases with increasing x, and the mole ratio of the tetrahedral site to the octahedral site is 1:0.33 at $x = 0.33$ (another end member). In this case MnO_2(Li) can be expressed as $(H)[H_{0.33}Mn_{1.67}^{4+}]O_4$, where (H) denotes the tetrahedral ion-exchange site and $H_{0.33}$ in [ ] denotes the octahedral ion-exchange site. According to Ooi et al. (8, 9), the lithium sorbing mechanisms of the two end members are expressed as

$$(\ )[Mn_2^{4+}]O_4 + Li^+ \rightarrow (Li)[Mn^{3+}Mn^{4+}]O_4 \tag{1}$$

and

$$(H)[H_{0.33}Mn_{1.67}^{4+}]O_4 + 1.33Li^+ \rightarrow (Li)[Li_{0.33}Mn_{1.67}^{4+}]O_4 \tag{2}$$

Sorbents with different *x* values are reported to show different characteristics as sorbents of ions (10). Hence, it could be possible that they also exhibit different lithium isotope effects. In this context, we prepared lithium manganese oxides with varying Li/Mn ratios, prepared sorbents from them by extracting lithium ions, and carried out characterization of the sorbents thus obtained, with the main focus on their lithium isotope selectivity. In this paper we report the results of such characterization.

EXPERIMENTAL

Lithium manganese oxides, the precursors, with the predetermined Li/Mn ratios were prepared from lithium carbonate and manganese carbonate. The weighed amounts of the two chemicals were well mixed and heated at a prefixed temperature in an electric furnace under an O_2 flow for 4 hours. The heating time of 4 hours was determined by preliminary experiments. The Li/Mn ratios were 0.42, 0.50, 0.70, and 0.84. The precursors with Li/Mn ratios of 0.50 and 0.70 should have the spinel-type structure. Those with Li/Mn ratios of 0.42 and 0.84, especially those with the Li/Mn ratio of 0.42, necessarily contain phases other than the spinel. The heating temperature was set at either 400, 600, or 850°C. In this paper we distinguish various precursors by the symbols PR-xx-yy, where xx denotes the approximate Li/Mn ratio and yy denotes the heating temperature.

The experimental values of the Li/Mn ratios were determined by decomposing aliquots of the precursors by a mixture of 1 M HCl and 30% H_2O_2 solution and then measuring the lithium and manganese concentrations of the resultant solutions by flame photometry and atomic absorption spectrometry, respectively. Judging from the precision of the spectroscopic methods used, the values of Li/Mn ratios with two figures after the decimal point were justified.

The sorbents were prepared by extracting lithium from the precursors with ammonium peroxodisulfate at 90°C as before (6). Their specific surface areas were typically 50–70 m^2/g as measured by the BET method. We express the sorbents as EX-xx-yy, corresponding to the precursors PR-xx-yy.

Identification of crystal phases in precursors and sorbents was carried out by powder x-ray diffraction (XRD).

To examine alkali metal ion selectivity of each sorbent, distribution coefficients (K_d) were measured. A 0.1-g aliquot of the sorbent was placed in 25 cm^3 of a buffer solution (0.2 M NH_4OH + 0.2 M NH_4Cl; pH 9.2) containing lithium, sodium, potassium, and rubidium ions, each at 1.0 mM. After equilibrium was reached, the concentrations of metal ions were measured and the amounts of ions taken up by the sorbent were calculated from the concentration differences before and after equilibrium. The K_d (cm^3/g) values defined as

$$K_d = \frac{\text{amount of ion sorbed per 1 g of sorbent}}{\text{amount of ion remaining per 1 cm}^3\text{ buffer solution}}$$

were then calculated.

The lithium isotope selectivity of a sorbent was measured batchwise at 25°C. A 0.1-g aliquot of the sorbent was placed in 10 cm^3 of 0.1 M LiOH solution with lithium of the natural isotopic composition. After equilibrium was attained, the sorbent was separated from the solution by filtration. The sorbent was then decomposed with a mixture of 0.1 M HCl and 30% H_2O_2 solution. The resultant solution was passed through a H^+-form cation-exchange column. Lithium ions taken up by the ion exchanger were eluted out of the column with 0.05 M HCl solution whereas Mn^{2+} ions from the sorbent remained in the column. The lithium ions were thus isolated and recovered as lithium chloride. The chemical form of lithium was changed to lithium iodide through anion exchange and the addition of HI, and the lithium iodide solution thus obtained was subjected to mass spectrometry to determine the ^{7}Li/^{6}Li isotopic ratio. Lithium in the solution phase after equilibrium was similarly converted to LiI for mass spectrometric lithium isotopic ratio measurements.

The procedure of lithium isotopic ratio measurements used was described in a previous paper (11). The mass spectrometer used was a MAT CH-5 at the Tokyo Institute of Technology or a Finnigan MAT-261 at the National Defense Academy.

The magnitude of lithium isotope selectivity was evaluated in terms of the ^{7}Li/^{6}Li isotopic separation factor, *S*, defined as

$$S = (^7\text{Li}/^6\text{Li})_{\text{solution}}/(^7\text{Li}/^6\text{Li})_{\text{sorbent}}$$

where $(^7\text{Li}/^6\text{Li})_{\text{solution}}$ and $(^7\text{Li}/^6\text{Li})_{\text{sorbent}}$ are the isotopic ratios in the solution and sorbent phases, respectively. By definition, the *S* value is larger than unity when the sorbent exhibits selectivity for ^{6}Li; that is, when ^{6}Li is preferentially fractionated into the sorbent.

RESULTS AND DISCUSSION

We show the XRD patterns of the selected precursors in Fig. 1. When the Li/Mn ratio is 0.50 [Fig. 1(c)] or 0.70 [Fig. 1(b)], only the spinel phase is observed, as expected. The sample with a Li/Mn ratio of 0.84 [Fig. 1(a)] contains Li_2MnO_3 as an impurity, probably due to the excessive Li content. Contrary to this, when the Li/Mn ratio is 0.42 [Fig. 1(d)], a γ-MnO_2 phase is detected, probably as a result of excessive Mn. The XRD peaks at a heating temperature

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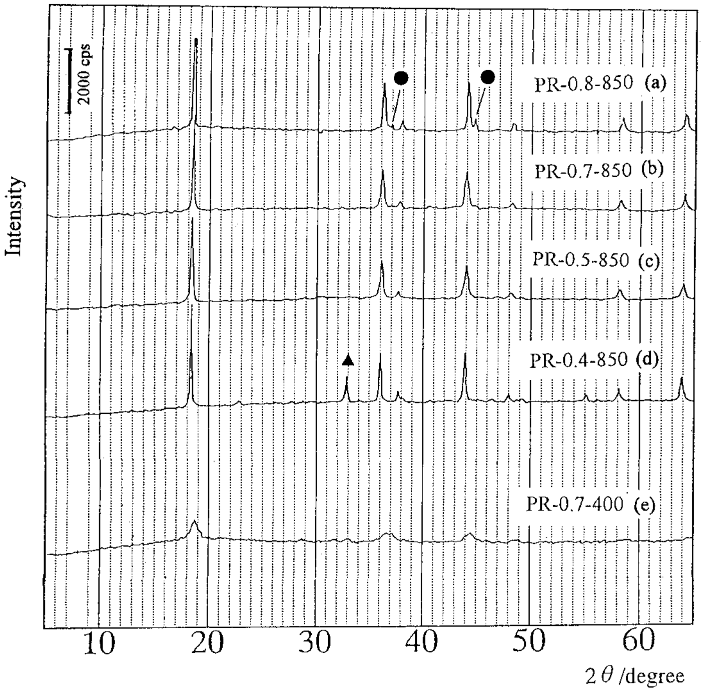

FIG. 1 XRD patterns of selected precursors. (a) PR-0.8-850; (b) PR-0.7-850; (c) PR-0.5-850; (d) PR-0.4-850; (e) PR-0.7-400. (●) Peaks of Li_2MnO_3; (▲) peak of γ-MnO_2. Peaks without marks are those of the spinel phase.

of 400°C are all small, as exemplified in Fig. 1(e). Identification of the spinel-type structure is narrowly possible, but the existence of the impurity phase is hard to judge. We tried in vain to promote crystal growth by increasing the heating time. A heating temperature of 400°C is evidently too low for the crystal to grow. This result is a contrast to the results by Feng et al. (12) who reported quite clear and sharp XRD patterns of precursors prepared at 400°C.

The degrees of Li extraction (%) from precursors are tabulated on the fourth column of Table 1. They are 80% or higher, and in many cases lithium is extracted practically completely. There is a general tendency for the degree of Li extraction to be lower for precursor prepared at higher temperatures except for the series of precursors with a Li/Mn ratio of 0.50. Table 1 also lists the degrees of Mn dissolution. There is little dissolution of manganese irrespective of the precursor.

The XRD patterns of selected sorbents are shown in Fig. 2. It is seen that the sorbents retain the spinel-type structure the precursors possess. Although not shown, the XRD patterns of different aliquots of one sample are in principle equivalent to each other, indicating that the samples are homogeneous. A comparison of Fig. 1(a) with Fig. 2(a) and of Fig. 1(d) with Fig. 2(c) indicates that impurities such as Li_2MnO_3 and γ-MnO_2 have been eluted out during the

TABLE 1
Degrees of Li Extraction and Mn Dissolution and Separation Factor

Sorbent	Precursor	Li/Mn ratio	Degree of Li extraction (%)	Degree of Mn dissolution (%)	*S*
EX-0.4-400	PR-0.4-400	0.42	100	0.02	1.0061
EX-0.4-600	PR-0.4-600	0.42	100	0.17	1.0079
EX-0.4-850	PR-0.4-850	0.42	92	0.02	1.0079
EX-0.5-400	PR-0.5-400	0.50	95	0.02	1.0092
EX-0.5-600	PR-0.5-600	0.50	100	0.02	1.0072
EX-0.5-850	PR-0.5-850	0.50	100	0.03	1.0088
EX-0.7-400	PR-0.7-400	0.70	100	0.02	1.0053
EX-0.7-600	PR-0.7-600	0.70	—	—	1.0062
EX-0.7-850	PR-0.7-850	0.70	93	0.02	1.0057
EX-0.8-400	PR-0.8-400	0.84	100	0.03	1.0040
EX-0.8-600	PR-0.8-600	0.84	98	0.03	1.0050
EX-0.8-850	PR-0.8-850	0.84	80	0.03	—

ammonium peroxodisulfate treatment. In some sorbents the formation of cryptomelane-type manganese oxide is traced at around $2\theta = 12°$.

It is difficult to discuss quantitatively the amounts of tetrahedral and octahedral sorption sites of the individual sorbents from only our experimental data. Equations (1) and (2) show that the lithium uptake should increase with an increasing Li/Mn ratio and with an increasing proportion of octahedral sites. The amounts of lithium ions taken up by the sorbents EX-xx-600 from 0.10 M LiOH solution are 2.91, 3.59, 3.65, and 4.88 mmol/g at xx = 0.4, 0.5, 0.7, and 0.8, respectively, at 25°C. These results support the view that sorbents with larger Li/Mn ratios have a larger proportion of octahedral sites.

We depict the selectivity of selected sorbents for alkali metal ions as K_d values in Fig. 3. As is seen, all of the sorbents are lithium-specific, with K_d values for the lithium ion varying slightly from sorbent to sorbent. It is difficult to detect any correlation between selectivity for alkali metal ions other than the lithium ion and preparation conditions of the sorbents such as Li/Mn ratio and heating temperature.

The values of *S* are listed in the last column of Table 1. They range from 1.0040 to 1.0092, showing the sorbents are all ^{6}Li-specific. Their errors are typically ±0.0006. The present maximum value of 1.0092 is inferior to the best *S* value obtained for the sorbents obtained from $LiMn_2O_4$ under various preparation conditions (6) and is equivalent to the value obtained for the sorbent prepared form $MgMn_2O_4$ (4).

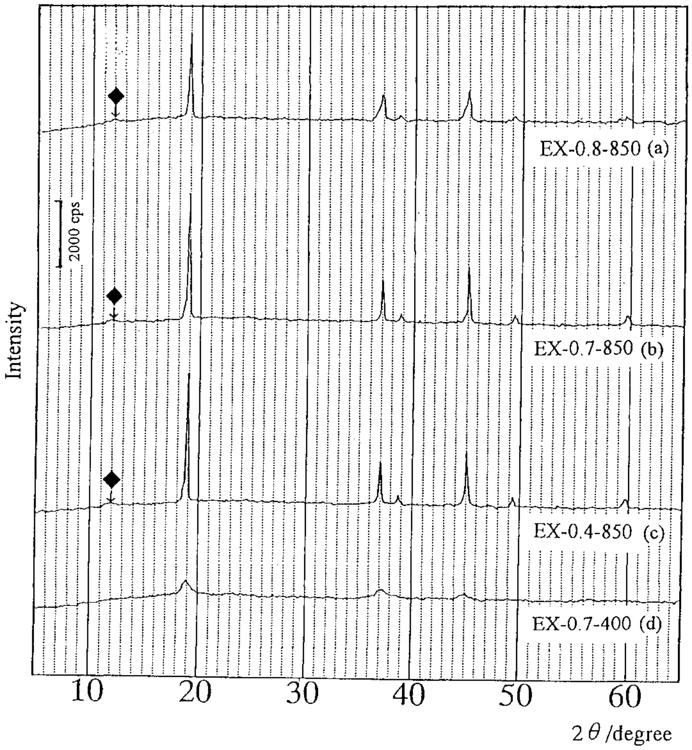

FIG. 2 XRD patterns of selected sorbents. (a) EX-0.8-850; (b) EX-0.7-850; (c) EX-0.4-850; (d) EX-0.7-400. (◆) Peaks of cryptomelane-type manganese oxide. Peaks without marks are those of the spinel phase.

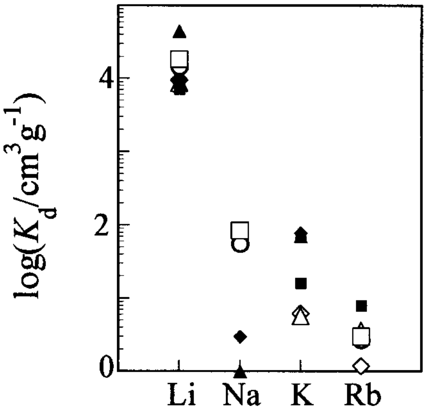

FIG. 3 Distribution coefficients of alkali metal ions at 25°C. (◇) EX-0.4-400; (△) EX-0.5-400; (○) EX-0.7-400; (□) EX-0.8-400; (◆) EX-0.4-600; (▲) EX-0.5-600; (●) EX-0.7-600; (■) EX-0.8-600

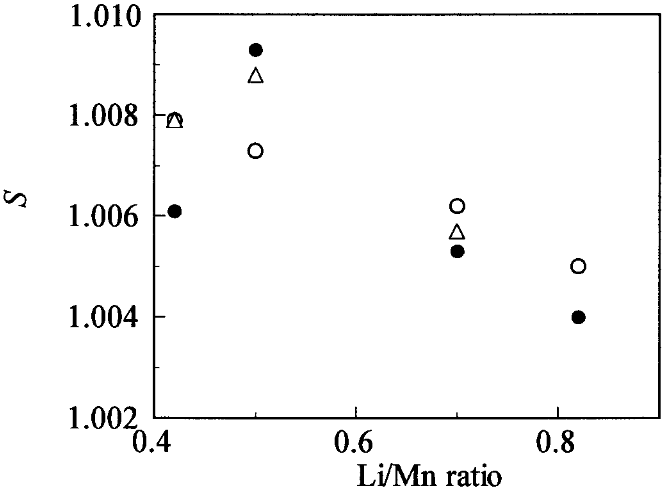

FIG. 4 Plot of *S* against Li/Mn ratio. (●) EX-xx-400; (○) EX-xx-600; (△) EX-xx-850.

The *S* values are plotted as a function of Li/Mn ratio in Fig. 4. The dependence of *S* on the heating temperature seems inconsistent. For example, *S*(heating temperature = 400) is smaller than *S*(600) at Li/Mn = 0.42, while *S*(400) is larger than *S*(600) at Li/Mn = 0.50. This inconsistency may be meaningful, but at present we have no reasonable explanation for it. We certainly need more data points. On the contrary, the *S* value is slightly dependent on the Li/Mn ratio; it has a maximum at a Li/Mn ratio of 0.50 and decreases as the Li/Mn ratio deviates from this value. The common solution phase is 0.1 M LiOH solution in the present systems, and hence the circumstance in which lithium ions reside in the solution phase is practically the same in all the experiments. Thus, the Li/Mn ratio dependence of *S* is attributable to the difference in environments around the lithium ion in the sorbent phase.

In the spinel-type structure, lithium ions are taken up into the tetrahedral or octahedral sorption sites formed by four and six oxide ions, respectively. The proportion of octahedral site increases with increasing Li/Mn ratio. Ideally, the ratio of the amount of tetrahedral sites to octahedral sites is 1:0 at a Li/Mn ratio of 0.50, while the ratio is 1:0.33 at a Li/Mn ratio of 0.80. The experimental *S* is given as the concentration-weighted average of the separation factor between the tetrahedral site and the solution phase [*S*(tetra/sol)] and that between the octahedral site and the solution phase [*S*(octa/sol)]. Thus, the present results can be best understood by assuming that *S*(tetra/sol) is larger than *S*(octa/sol), or equivalently, lithium ions are more stable in octahedral sites than in tetrahedral sites. This assumption is consistent with a previous experimental result (13).

The fact that *S* is larger for a Li/Mn ratio of 0.5 than for a Li/Mn ratio of 0.4 may be ascribed to distortion of the sorption site. Ideally, both EX-0.5-yy and

EX-0.4-yy possess only tetrahedral sorption sites. Since the impurity that is absent from EX-0.5-yy exists in PR-0.4-xx and it is eluted out in the preparation process, it is quite possible that the sorption sites of EX-0.4-yy are distorted more substantially than those of EX-0.5-yy. The sum of forces acting on a lithium ion is then expected to be larger in the more distorted tetrahedral site than in the less distorted site. This is because one of the four oxide ions forming the sorption site can be located closer to the lithium ion in the distorted structure than in the nondistorted structure. The larger sum of forces acting on lithium ions in sorbents leads to a smaller *S* value, based on the classical isotope effect theory (14).

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