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Extraction of Lithium from $LiMn_2O_4$ by Ammonium Peroxodisulfate and Lithium Isotope Selectivities of Adsorbents Thus Obtained

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ABSTRACT

Extraction of lithium ions from $LiMn_2O_4$ by ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) was studied, and properties of adsorbents thus obtained ($MnO_2(Li)$) were examined with a special focus on their ability to separate the lithium isotopes. Under well-controlled conditions, $(NH_4)_2S_2O_8$ was an excellent lithium ion extractant, with satisfactorily high degrees of lithium extraction while maintaining minimal dissolution of manganese. The maximum value of the $^7Li/^6Li$ isotopic separation factor with $MnO_2(Li)$ thus prepared was 1.014 at 25°C, which was several times larger than those of commercially available organic ion-exchangers.

INTRODUCTION

Lithium is an element that has drawn attention in recent years due to its potentially wide applications in industry. It is used as a raw material in materials such as ceramics, medicines, and dry batteries, and will be used in aluminum-based alloys and large-capacity batteries in the near future (1, 2). In addition, isotopically pure or enriched lithium (^6Li and ^7Li) has applications in nuclear science and industry (nuclear fusion and nuclear fission). The overall consumption of lithium is expected to grow worldwide.

Responding to the expected growth in lithium demand, lithium-specific adsorbents which have extremely high affinity toward lithium ions have

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been developed, and studies on lithium recovery from seawater and/or geothermal water rich in lithium using such adsorbents have been carried out (3–7). Other than lithium recovery, one of their important applications could also be for lithium isotope separation. If they have high selectivities not only for lithium but also for the lithium isotopes (^{6}Li or ^{7}Li), they could be used to separate the lithium isotopes as they are recovering lithium (8), thus satisfying the demand both for elemental lithium and for the lithium isotopes.

The adsorbent (hereafter designated as MnO_2(Li)) prepared by extracting lithium from $LiMn_2O_4$ is one of the promising lithium-specific adsorbents in which lithium ions are considered to be taken up on the sites which lithium had occupied in $LiMn_2O_4$. Hydrochloric acid or nitric acid solution had been used to remove the lithium from $LiMn_2O_4$. A disadvantage of HCl and HNO_3 as lithium extractants is that, although the degree of lithium extraction is high, the degree of manganese dissolution is also high (9). To limit the degree of Mn dissolution during the preparation of MnO_2(Li) while keeping a high degree of lithium extraction, we used ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) solutions as the Li extractant. In this paper we first describe the preparation of MnO_2(Li) using $(NH_4)_2S_2O_8$ and then discuss some properties of the products produced, with a special focus placed on the lithium isotope effects they show.

EXPERIMENTAL

Preparation of the Adsorbent

The precursor of the adsorbent, $LiMn_2O_4$, was synthesized by heating a mixture of $MnCO_3$ and Li_2CO_3 with the mole ratio of 4:1 at 850°C for 4 hours, following the method of Ooi (10, 11), and the product $LiMn_2O_4$ was identified by powder x-ray diffraction (XRD) spectroscopy as shown in Fig. 1(a). $LiMn_2O_4$ has a spinel structure with a cubic closed-packed oxygen framework (12). MnO_2(Li) was prepared by extracting lithium from $LiMn_2O_4$ using HCl, HNO_3, or $(NH_4)_2S_2O_8$. The conditions of lithium extraction were varied, and their effects on the characteristics of the adsorbents obtained were investigated. The adsorbents prepared under different conditions were identified by XRD spectroscopy; they all had XRD patterns similar to that of $LiMn_2O_4$ (10, 11).

The degree of manganese dissolution, DD_{Mn} (%), in each MnO_2(Li) preparation was calculated from the amount of manganese in the original $LiMn_2O_4$ aliquot, b (mg), and in the supernatant, c (mg), as

$$DD_{Mn} = 100 \times c/b$$

The degree of lithium extraction, DE_{Li} (%), was calculated from the amount of lithium in the original $LiMn_2O_4$ aliquot, q (mg), the amount in the supernatant, r (mg), and the DD_{Mn} (13).

$$DE_{\mathrm{Li}} = 100 \times [(100 \times r/q - DD_{\mathrm{Mn}})/(100 - DD_{\mathrm{Mn}})]$$

Characterization of MnO_2(Li) as Specific Lithium Adsorbent

In order to confirm that MnO_2(Li) prepared in the present work has properties of a specific lithium adsorbent comparable to those of MnO_2(Li) given in the literature, the following measurements were performed.

Amounts of Metal Ions Sorbed

A 0.1-g sample of the adsorbent was placed in 10 cm^3 of a 0.1 M (1 M = 1 mol/dm^3) metal hydroxide solution. After equilibrium was reached between the adsorbent and solution phases, the two phases were separated by filtration. The amount of the metal ion sorbed was determined by flame photometry after decomposition of the adsorbent with a mixture of 10 cm^3 0.1 M HCl and 1 cm^3 30% H_2O_2 solutions. The temperature was kept constant during the experiment.

Distribution Coefficients

A 0.1-g sample of the adsorbent was placed in 25.0 cm^3 of a buffer solution (0.2 M NH_4OH + 0.2 M NH_4Cl) of pH 9.18 which contained Li, Na, K, Rb, Mg, Ca, and Sr ions, each at 1.0 mM. After equilibrium was attained between the solution and adsorbent phases, the two phases were separated by filtration, and the amounts of each ion in the two phases were measured. The amount of an ion taken up by the adsorbent was calculated from the difference in its concentration in the solution phase before and after sorption. The distribution coefficient, K_d (cm^3/g), defined as

$$K_d = \frac{\text{the amount of the ion sorbed per 1 g of the adsorbent}}{\text{the amount of the ion remaining per 1 cm}^3\text{ of the supernatant}}$$

was calculated for each metal ion examined. The temperature was kept constant during the experiment.

Rate of Lithium Sorption

A 0.1-g sample of the adsorbent was placed in 10 cm^3 of a 0.1 M LiOH solution, and transfer of lithium ions from the solution to the adsorbent commenced immediately. A small volume of the solution was sampled periodically, and the lithium concentration in it was measured. The temperature of the solution was kept constant during the experiment.

Characterization of $MnO_2(Li)$ as a Lithium Isotope Separator

Overall Lithium Isotope Effects

The lithium isotope selectivity of $MnO_2(Li)$ prepared in this work was measured batchwise at a given temperature. A 0.1 g (or 0.2 g) sample of the adsorbent was placed in 10 cm^3 (or 20 cm^3) of a 0.1 M LiOH solution. After equilibrium was attained, the adsorbent was separated from the supernatant by filtration. The adsorbent was decomposed with a mixture of 0.1 M HCl and 30% H_2O_2 solution. The resultant solution was passed through a cation-exchange column packed with Muromac 50W-X8 resin in the H^+ form; the cations (Li^+ and Mn^{2+}) were adsorbed onto the resin. Lithium ions were eluted out of the column with 0.05 M HCl, but manganese ions remained in the column. Thus the lithium ions were isolated and recovered as lithium chloride. The chemical form of the isolated lithium was then changed to lithium iodide through anion exchange and was subjected to mass spectrometry to determine the $^7Li/^6Li$ isotopic ratio. Lithium in the supernatant was similarly changed to LiI for mass spectrometry.

A MAT CH-5 mass spectrometer and a surface ionization technique were used to determine the $^7Li/^6Li$ isotopic ratio of a sample as described in a previous paper (14). The $^7Li/^6Li$ determination was briefly as follows. After the ion beam intensities of $^6Li^+$ and $^7Li^+$ became sufficiently high, the ^6Li and ^7Li mass peaks were recorded repeatedly. The mass scanning was repeated several times in a block, and several blocks were recorded as one measurement. The value of the $^7Li/^6Li$ ratio of a block was calculated by averaging all the peak-height ratios in the block, and that of the measurement was calculated as the average of the values of the $^7Li/^6Li$ ratios of the blocks. The relative standard deviation of a $^7Li/^6Li$ measurement was calculated using the $^7Li/^6Li$ ratios of the blocks and was typically 0.1%. The $^7Li/^6Li$ of a sample was usually the result of one measurement, but whenever we felt the relative standard deviation was too large, we made extra measurement(s) on that sample. In those cases, the $^7Li/^6Li$ value and the relative standard deviation were the result of multiple measurements. The initial value of the $^7Li/^6Li$ ratio in the lithium chemical (LiOH) used in this work was 12.42.

To estimate the magnitude of the lithium isotope effect from the adsorbent, the $^7Li/^6Li$ isotopic separation factor, S, was evaluated,

$$S = (^7Li/^6Li)_{sol}/(^7Li/^6Li)_{ads}$$

where $(^7Li/^6Li)_{sol}$ and $^7Li/^6Li)_{ads}$ are the $^7Li/^6Li$ isotopic ratios in the solution and sorption phases, respectively. By definition, the S value is larger than unity when the heavier isotope, ^7Li, is preferentially fractionated into the solution phase; that is, when the adsorbent shows a selectivity for the lighter isotope, ^6Li. The error in S value was estimated from the errors in $(^7Li/^6Li)_{sol}$ and $(^7Li/^6Li)_{ads}$ and in the amount of lithium ions not extracted from $LiMn_2O_4$.

Lithium Isotope Effects of Different Sorption Sites

Besides batch equilibration experiments, elution experiments were performed to determine whether $MnO_2(Li)$ has different kinds of sorption sites and, if so, whether the different sites show different lithium isotope effects. A 0.1-g sample of the adsorbent was first placed in 10 cm^3 of a 0.1 M LiOH solution. After equilibrium was attained, the adsorbent was separated from the supernatant by filtration as before. After the adsorbent was packed in a small column, it was washed with 0.001 M HCl. Then it was washed with 0.01 M HCl, followed by a wash with 0.05 M HCl. After washing with 0.05 M HCl, almost all the lithium ions sorbed were eluted. (Similar results were obtained with 0.1 M HCl and 0.5 M $(NH_4)_2S_2O_8$.) The amount of lithium and the $^7Li/^6Li$ isotopic ratio of each effluent were measured. Using the $^7Li/^6Li$ value of the supernatant and those of the effluents, we calculated the S values and estimated the magnitudes of the lithium isotope effects of the different sorption sites.

RESULTS AND DISCUSSION

Preparation of $MnO_2(Li)$

The conditions of Li extraction from $LiMn_2O_4$ and the DE_{Li} and DD_{Mn} values obtained are summarized for the selected $MnO_2(Li)$ preparation experiments in Table 1, and the XRD patterns of selected $MnO_2(Li)$ samples prepared are shown in Fig. 1, together with that of $LiMn_2O_4$ (Fig. 1a). The peak positions in the XRD patterns of $MnO_2(Li)$ (marked with open circles in Fig. 1) agree well with those given in the literature (10). The following information could be extracted from the table and figure.

1. Runs T01 and E01 differ only in the $(NH_4)_2S_2O_8$ concentration. Although the DE_{Li} values are satisfactorily high in both cases, the DD_{Mn}

value of E01 is much higher than that of T01, and impurity peaks are observed in the XRD pattern of E01 (marked with open triangles in Fig. 1c). Thus, 0.1 M is too low for $(NH_4)_2S_2O_8$ to extract Li adequately, but 0.5 M $(NH_4)_2S_2O_8$ is a good Li extractant under the experimental conditions examined.

2. Runs T01 and E02 are different only in that the $(NH_4)_2S_2O_8$ solution was used immediately after its preparation in T01 while the extractant was used more than 10 days after its preparation in E02. Although the DE_{Li} value is sufficiently high and the Mn dissolution is satisfactorily suppressed in E02, the formation of the cryptomelane-type manganese oxide, which shows a high selectivity for potassium and rubidium ions rather than for lithium ions (15, 16), is observed on the XRD pattern of the adsorbent of E02 (marked with a filled triangle in Fig. 1d). This suggests that $(NH_4)_2S_2O_8$ solution should be prepared immediately before its use.
3. Run T03 is identical to Run T01 except that the extraction time was 3 hours in T03 while it was 1 hour in T01. No substantial difference in DE_{Li}, DD_{Mn}, or XRD pattern is observed between the two experiments. The extraction time of 1 hour is thus sufficient when the Li extractant is 0.5 M $(NH_4)_2S_2O_8$ solution and the temperature is 90°C.
4. $MnO_2(Li)$ was prepared at a lower temperature (25°C) in Run L12. Since the DE_{Li} value was very low at the extraction time of 1 hour, we continued the experiment up to the extraction time of 10 hours.

TABLE 1
Preparation Conditions of $MnO_2(Li)^a$ and the Degrees of Li Extraction and Mn Dissolution

Run	Li extractant	Extraction time (h)	Temperature (°C)	Degree of Li extraction (%)	Degree of Mn dissolution (%)	Fig.
T01	0.5 M $(NH_4)_2S_2O_8$	1	90	93.9	0.24	1(b)
E01	0.1 M $(NH_4)_2S_2O_8$	1	90	93.7	4.57	1(c)
E02	0.5 M $(NH_4)_2S_2O_8{}^b$	1	90	91.7	0.01	1(d)
T03	0.5 M $(NH_4)_2S_2O_8$	3	90	93.2	0.23	
L12	0.5 M $(NH_4)_2S_2O_8$	10	25	85.4	0.01	
E04	0.1 M HCl	1	90	87.3	24.3	
E06	1.0 M HCl	1	90	85.3	30.1	1(e)
E07	0.1 M HNO_3	1	90	86.4	25.8	
E09	1.0 M HNO_3	1	90	83.3	28.8	

[a] 0.1 g of $LiMn_2O_4$ was treated with 10 cm^3 of the extractant.
[b] Used more than 10 days after its preparation.

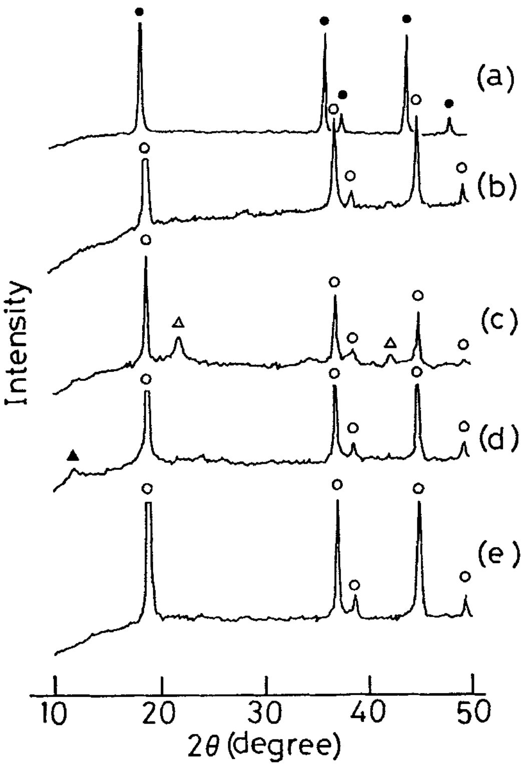

FIG. 1 Powder x-ray diffraction patterns of $LiMn_2O_4$ and $MnO_2(Li)$ samples. The preparation conditions of the $MnO_2(Li)$ samples are summarized in Table 1. (●) Peaks of $LiMn_2O_4$; (○) peaks of $MnO_2(Li)$; (△) peaks of impurity; (▲) peak of cryptomelane-type manganese oxide.

While the DD_{Mn} value was kept low, the DE_{Li} value was lower than those of the other runs using $(NH_4)_2S_2O_8$ even at the extraction time of 10 hours. $(NH_4)_2S_2O_8$ solution thus works as a Li extractant more actively at a higher temperature.

5. Compared with $(NH_4)_2S_2O_8$ solutions, HCl solutions yield large DD_{Mn} values (ca. 30%). In addition, a trend was found. The DD_{Mn} value increases slightly and the DE_{Li} value decreases slightly with the increase in HCl concentration, although this is not shown very clearly in Table 1. A large DD_{Mn} value from HCl is a disadvantage of HCl as the Li extractant. In the XRD patterns, however, no peaks other than those attributable to $MnO_2(Li)$ are detected (cf. Fig. 1e), irrespective of HCl concentration. Thus, although the use of HCl results

in a relatively high Mn dissolution, the purity of $MnO_2(Li)$ obtained by x-ray spectroscopy is not dependent on the Li extraction conditions within the experimental range examined, and strict control of experimental conditions is not necessary. Similar observations can be made for the experiments with HNO_3 solutions as the Li extractant.

Although not shown in Table 1, Li extraction experiments were also conducted in which the Li extraction treatments with $(NH_4)_2S_2O_8$ were repeated. In all the cases, more than 98% of the total extracted Li was removed by the first treatment, and no appreciable further amount of Li was extracted in the third extraction treatment. In the preparation of $MnO_2(Li)$ used for various characterizations to be described below, the extraction treatment was usually repeated twice for the sake of caution.

$(NH_4)_2S_2O_8$ is superior to HCl and HNO_3 as a Li extractant in that it can extract Li in a high degree (usually over 90%) while suppressing Mn dissolution (less than 1%). It reacts in aqueous solutions as (17)

$$2(NH_4)_2S_2O_8 + 2H_2O \rightarrow 4NH_4HSO_4 + O_2 \qquad (1)$$

$$NH_4HSO_4 \rightarrow NH_4SO_4^- + H^+ \qquad (1')$$

O_2 in Eq. (1) works as an oxidant, preventing the dissolution of manganese, while H^+ in Eq. (1′) acts as an acid, extracting Li^+ from $LiMn_2O_4$. For $(NH_4)_2S_2O_8$ to work effectively as a Li extractant, the balance between the acid and oxidant properties is important. If the acid strength is superior to the oxidant strength, a high DE_{Li} value would be achieved at the sacrifice of DD_{Mn}. On the contrary, if the relative strengths are reversed, the Mn dissolution would be suppressed with an unsatisfactorily low DE_{Li} value. The best conditions in the present experiments are: for the weight of $LiMn_2O_4$/the volume of the extractant ratio to be approximately 10 g/dm^3; for the concentration of $(NH_4)_2S_2O_8$ to be 0.5 M; for the temperature to be 90°C; for the extraction time to be approximately 1 hour; and for the number of extraction treatments to be 2. The extractant should be prepared immediately before its use.

$(NH_4)_2S_2O_8$ solution was also successfully used to extract magnesium from $MgMn_2O_4$ (13) and Mg_2MnO_4 (17) in preparations of other manganese-oxide-based lithium-specific adsorbents.

Characterization of $MnO_2(Li)$ as Specific Lithium Adsorbent

Amounts of Metal Ions Sorbed

The amounts of lithium, sodium, and potassium ions sorbed were, respectively, 4.61–5.47, 0.03–0.70, and 0.19–0.71 meq per 1 g of adsorbent at 25°C, varying slightly depending on preparation conditions. However, as is shown in Table 3, the adsorbents prepared under equivalent conditions showed approximately the same lithium uptake for the same Li concentration of the solution phase. The lithium uptake observed in this work is about the same as that estimated in the literature (18).

Although the amounts of sodium and potassium ions sorbed are very small compared with the uptake of the lithium ions, sorption of these ions indicates the existence of adsorption sites which are not lithium-specific. Those adsorption sites are probably located on the surface of the adsorbent, since the sodium and potassium ions cannot enter the inside of the adsorbent due to size exclusion (10). On the contrary, the high lithium uptake data strongly indicate that lithium ions can enter the interior of the adsorbent as has previously been claimed (10, 19); that is, in a strict terminology, lithium ions are both adsorbed and "absorbed" by the adsorbent. There is supporting evidence for this. Table 2 shows the values of the lattice constants, a_0, of the precursor $LiMn_2O_4$ and the adsorbent $MnO_2(Li)$ before and after the uptakes of lithium and potassium ions. The lattice constants are calculated from the peak positions at around $2\theta = 18°$ on the XRD patterns. The value of a_0 of the $LiMn_2O_4$ is 8.32 Å, and by extracting lithium ions it shrinks to 8.06–8.08 Å (the adsorbent). After the uptake of lithium ions, the a_0 value of the adsorbent became 8.34 Å; that is, it was restored to the value of the precursor. By contrast, after the adsorption of potassium ions, the a_0 value of the adsorbent was unchanged at 8.08–8.10 Å. A similar a_0 change with lithium sorption was also previously reported (19).

TABLE 2

Lattice Constants, a_0, of $LiMn_2O_4$ and $MnO_2(Li)$ Before and After Li^+ and K^+ Uptakes

	a_0 (Å)			
Run	$LiMn_2O_4$	$MnO_2(Li)$	After Li^+ uptake[a]	After K^+ uptake[b]
L08[c]	8.32	8.08	8.34	8.10
L10[d]	8.32	8.06	8.34	8.08

[a] The weight of the adsorbent was 0.1 g. The solution phase was 10 cm^3 of 0.1 M LiOH aqueous solution.

[b] The weight of the adsorbent was 0.1 g. The solution phase was 10 cm^3 of 0.1 M KOH aqueous solution.

[c] The adsorbent was prepared under the conditions of Run T01 of Table 1 except that $(NH_4)_2S_2O_8$ was used a couple of days after its preparation.

[d] The adsorbent was prepared under the conditions of Run E06 of Table 1 except that the extraction time was 30 minutes.

The lithium uptake increases slightly with temperature between 5 and 70°C. This positive temperature dependence has also been reported for the adsorbent prepared from Mg_2MnO_4 (17).

Distribution Coefficients

The distribution coefficients of the alkali and alkaline earth metal ions are plotted for three $MnO_2(Li)$ samples obtained under different preparation conditions in Fig. 2. Although the three adsorbents often show different K_d values for the metal ions other than the lithium ion, they have equivalently high selectivities for the lithium ion among the alkali and alkaline earth metal ions.

The results of the measurements of metal ion uptakes and distribution coefficients of the metal ions show that the adsorbents prepared in this work have good selectivity for lithium and satisfactorily large lithium ion uptakes as long as their XRD patterns agree with that given in the literature (10, 11) and the degrees of lithium extraction during their preparations from $LiMn_2O_4$ are high.

Rate of Lithium Sorption

The amount of lithium taken up by the adsorbent is plotted against time in Fig. 3. Equilibrium is reached in about 12 hours at 50°C and in about 2 days at 25°C. These times are long compared with those obtained with

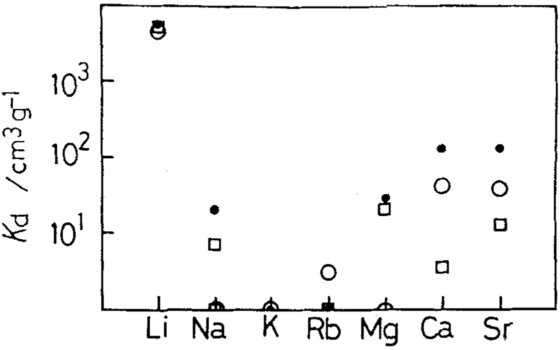

FIG. 2 Distribution coefficients of alkali and alkaline earth metal ions. (●) The adsorbent was prepared under the conditions of Run T01 of Table 1 except that $(NH_4)_2S_2O_8$ was used a couple of days after its preparation. (○) The adsorbent was prepared under the conditions of Run E06 of Table 1 except that the extraction time was 30 minutes. (□) The adsorbent was prepared under the conditions of Run E06 of Table 1 except that the HCl concentration was 2.0 M and the extraction time was 30 minutes.

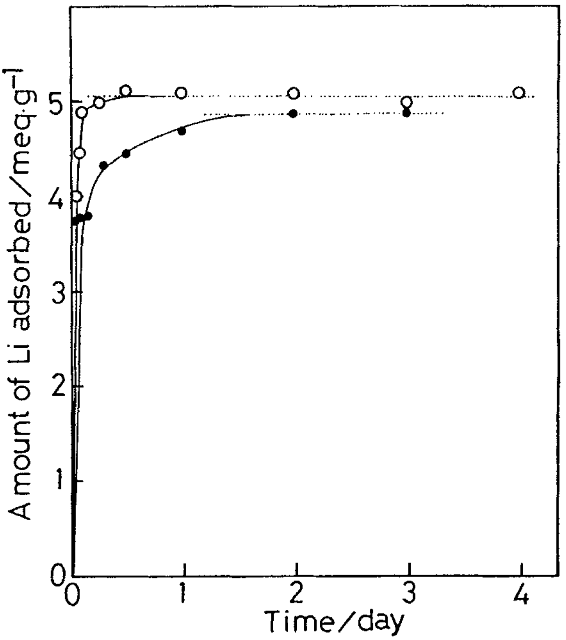

FIG. 3 Plot of the amount of lithium ion sorbed (meq per 1 g of adsorbent) against reaction time. Temperature: 50°C (○); 25°C (●).

commercially available organic ion-exchange resins; For example, Dowex 50-8X (100–200 mesh) and CA LS-6 (100–200 mesh), respectively, have equilibrium times of 5 hours and 50 minutes at 25°C in similar experiments (unpublished data from the authors). $MnO_2(Li)$ prepared in the present work is thus slow in sorption and/or ion-exchange reaction and would need to be improved for $MnO_2(Li)$ to become an acceptable lithium adsorbent for commercial operations.

Lithium Isotope Effects

In every batch experiment the *S* value was always larger than unity. Thus, $MnO_2(Li)$ is isotopically ^6Li-specific, with the lighter isotope ^6Li being preferentially taken up by $MnO_2(Li)$.

Table 3 summarizes the results of the batch experiments carried out to examine the reproducibility of the lithium isotope effects. In each of the three series of experiments (1, 2, and 3), the *S* value is constant within experimental errors, confirming that adsorbents synthesized under the

TABLE 3
Reproducibility of Lithium Uptake and Lithium Isotope Effect[a]

Experiment	Degree of Mn dissolution (%)	Li uptake (meq/g)	S^b
1A[c]	0.06	4.74	1.014 ± 0.001
1B[c]	0.03	4.71	1.012 ± 0.001
1C[c]	—	4.71	1.014 ± 0.001
2A[d]	31.2	4.80	1.0067 ± 0.0011
2B[d]	28.2	5.12	—
2C[d]	26.7	5.11	1.0058 ± 0.0009
3A[e]	0.02	4.71	1.0086 ± 0.0010
3B[e]	0.02	4.86	1.0086 ± 0.0021
4A[f]	—	5.69	1.012 ± 0.003

[a] The weight of the adsorbent was 0.1 g (or 0.2 g). The solution phase was 10 cm^3 (or 20 cm^3) of 0.1 M LiOH aqueous solution except for Experiment 4A where the Li concentration was 3.3 M. The temperature was kept at 25°C.

[b] $S = (^7Li/^6Li)_{\text{solution phase}}/(^7Li/^6Li)_{\text{adsorbent phase}}$.

[c] The adsorbent of each run was independently prepared under the conditions of Run T01 of Table 1.

[d] The adsorbent of each run was independently prepared under the conditions of Run E06 of Table 1.

[e] The adsorbent of each run was independently prepared under the conditions of Run T01 of Table 1 except that the $(NH_4)_2S_2O_8$ concentration was 0.25 M and the extraction time was 30 minutes.

[f] The experimental conditions other than the Li concentration in the solution phase were the same as those of Experiment 1C.

equivalent conditions show the similar magnitudes of lithium isotope effects. Table 3 also shows that the magnitude of the lithium isotope effect observed for $MnO_2(Li)$ is influenced only very slightly (negatively) by changes in the lithium concentration between 0.1 and 3.3 M. (Compare Experiments 4A and 1C; different aliquots of the same adsorbent sample were used in the two experiments.)

In Fig. 4 the S values obtained at 25°C are plotted against the DD_{Mn} value in the $(NH_4)_2S_2O_8$ treatment of $LiMn_2O_4$. There appears to be a trend for the S value to decrease with increasing DD_{Mn} value, indicating that a larger lithium isotope effect is expected for $MnO_2(Li)$ with a less defective structure.

In Fig. 5, S values obtained for two $MnO_2(Li)$ adsorbents prepared under different conditions are plotted against temperature. The S value shows a tendency to decrease with increasing temperature for both adsor-

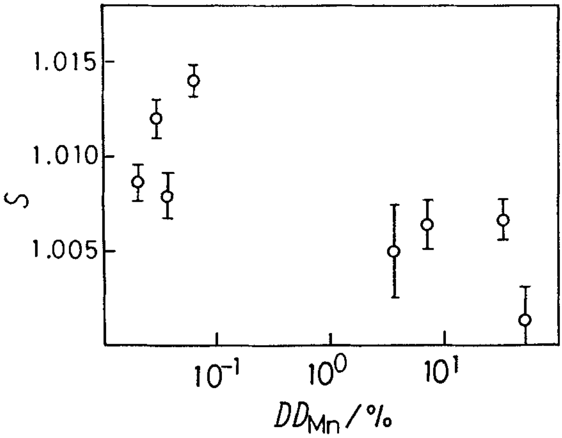

FIG. 4 Plot of the ^{7}Li/^{6}Li isotopic separation factor (S) against the degree of manganese dissolution (DD_{Mn}).

bents. The temperature dependence of the lithium isotope effect of $MnO_2(Li)$ is qualitatively consistent with that predicted by the classical theory of isotope effects (20).

The maximum S value obtained is 1.014 ± 0.001 at 25°C. This value should be compared with $S \sim 1.002$ obtained with commercially available

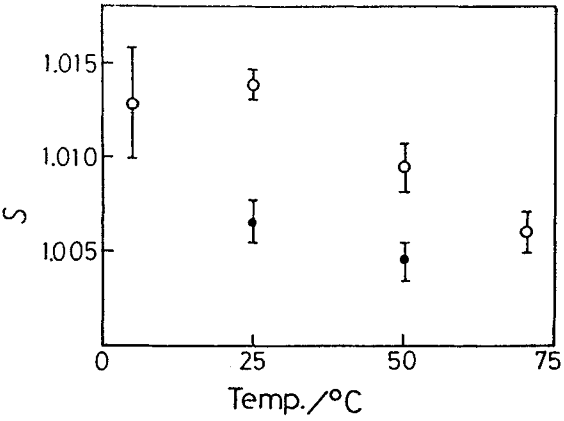

FIG. 5 Plot of the ^{7}Li/^{6}Li isotopic separation factor (S) against temperature. (○) The adsorbent was prepared under the conditions of Run T01 of Table 1 except that $(NH_4)_2S_2O_8$ was used a couple of days after its preparation. (●) The adsorbent was prepared under the conditions of Run E06 of Table 1.

ion exchangers (14). Since the importance of the isotope effect is evaluated by the magnitude of the deviation of the *S* value from unity, rather than the value of *S* itself, it follows that $MnO_2(Li)$ potentially has a lithium isotope separation ability several times higher than those of commercially available ion exchangers. However, *S* values obtained for the present systems with $MnO_2(Li)$ are still smaller than those of the systems with crown ethers (21–23) and with mercury amalgam (24).

In evaluating the feasibility of a lithium isotope separation system, the isotope exchange rate is another important factor, although this subject is beyond the scope of the present paper. We did not measure lithium isotope exchange rates over $MnO_2(Li)$. Judging from the results on the rate of lithium sorption in Fig. 3, it is expected to be slow, slower than those of organic ion exchangers. The lithium isotope exchange rates of systems with a crown (21) and with mercury amalgam (24) were reported to be about 30 seconds and about 60 seconds, respectively.

Lithium Isotope Selectivities of Different Sorption Sites

The results of the elution experiment are summarized in Table 4. The *S* value obtained between the supernatant and lithium elutable with 0.001 M HCl is 1.0018, which is essentially the same as those obtained for commercially available organic ion exchangers at 25°C (14). In addition, the amount of lithium eluted with 0.001 M HCl is 0.65 meq/g, which is about the same as that of sodium or potassium ion taken up by the adsorbent (vide supra). These facts suggest that the lithium ions eluted with 0.001 M HCl had been adsorbed on surface adsorption sites of the adsorbent which did not show high selectivity for the lithium ion.

TABLE 4
Separation Factor Values Assigned to Different Sorption Sites

Site	Amount of Li sorbed (meq/g)	S^a
Overall	4.71	1.014 ± 0.001
Surface[b]	0.65	1.0018 ± 0.0016
Lattice I[c]	1.20	1.0024 ± 0.0016
Lattice II[d]	2.86	1.021 ± 0.001

[a] $S = (^7Li/^6Li)_{solution}/(^7Li/^6Li)_{site}$.

[b] Lithium ions sorbed here were elutable with 0.001 M HCl.

[c] Lithium ions sorbed here were elutable with 0.01 M HCl.

[d] Lithium ions sorbed here were elutable with 0.05 M HCl but not with 0.01 M HCl.

Except for the lithium ions adsorbed on surface sites, lithium ions taken up by the adsorbent seem divided into two groups: those eluted out with 0.01 M HCl and those not eluted with 0.01 M HCl but eluted with 0.05 M HCl. The *S* values of the two groups are quite different from each other: 1.0024 and 1.021 at 25°C, respectively. These results suggest the existence of two different "absorption" sites inside the adsorbent. Goodenough et al. (25) proposed in a study of the electrochemical extraction of lithium ion from $LiMn_2O_4$ that there existed a stable species expressed as $Li_{0.5}Mn_2O_4$. Ooi et al. (19) speculated from a careful x-ray analysis that there were two different vacant sites in $MnO_2(Li)$. Our present results are consistent with the results of those previous works. In our study, the two absorption sites are distinguished by the difference in magnitude of lithium isotope selectivity.

In short, it is highly probable that there are three different adsorption and absorption sites on $MnO_2(Li)$. One is on the surface of $MnO_2(Li)$ and is not Li-specific. The other two are inside the cubic closed-packed oxygen framework. The three different kinds of sites are all ^6Li-specific but exhibit different magnitudes of lithium isotope effects.

CONCLUSION

Ammonium peroxodisulfate is an excellent lithium extractant in the preparation of $MnO_2(Li)$ from $LiMn_2O_4$. It can extract lithium ions at satisfactorily high degrees while keeping the degree of manganese dissolution sufficiently low. The optimum concentration of $(NH_4)_2S_2O_8$ is 0.5 M and the reaction temperature is 90°C. $MnO_2(Li)$ prepared using $(NH_4)_2S_2O_8$ as the lithium extractant has specific adsorbent characteristics for lithium equivalent to those prepared using HCl or HNO_3.

$MnO_2(Li)$ preferentially adsorbed ^6Li over ^7Li. The maximum isotopic separation factor is 1.014 at 25°C, a lithium isotope effect several times larger than those of commercially available organic ion exchangers.

There appear to be three different kinds of adsorption and absorption sites: one adsorption site on the surface and two absorption sites inside the adsorbent. The lithium isotope effects are quite different for the different sites.

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SYMBOLS

a_0	lattice constant of the cubic system (Å)
b	the amount of manganese in the original $LiMn_2O_4$ aliquot (mg)
c	the amount of manganese in the supernatant (mg)
DD_{Mn}	the degree of manganese dissolution (%)
DE_{Li}	the degree of lithium extraction (%)
K_d	distribution coefficient (cm^3/g)
$MnO_2(Li)$	adsorbent prepared from $LiMn_2O_4$
q	the amount of lithium in the original $LiMn_2O_4$ aliquot (mg)
r	the amount of lithium in the supernatant (mg)
S	the $^7Li/^6Li$ isotopic separation factor
XRD	powder x-ray diffraction

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