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Ion and lithium isotope selectivities of sorbents prepared from Mg_2MnO_4

NORIKO IZAWA, TAKAO OI*
Department of Chemistry, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102, Japan

A lithium-specific sorbent, HMnO(2Mg), has been prepared by extracting magnesium ions from Mg_2MnO_4 through ion exchange with hydrogen ions, and its ion and lithium isotope selectivities have been studied as functions of the degree of magnesium extraction, DE_{Mg}. The properties as a specific-lithium sorbent revealed itself for the sorbents with a DE_{Mg} value of over 50%. The maximum distribution coefficient for the lithium ion and the maximum lithium uptake from a 0.1 M LiOH solution were 14900 $cm^3\,g^{-1}$ and 2.26 $mmol\,g^{-1}$, respectively, at $DE_{Mg} = 97\%$ at 25 °C. Isotopically, HMnO(2Mg) was a ^6Li-specific sorbent like other inorganic sorbents and organic ion exchangers so far investigated. The ^7Li-to-^6Li isotopic separation factor varied between 1.006 and 1.016 at 25 °C as a function of DE_{Mg}. High ^6Li selectivity was observed when HMnO(2Mg) did not show properties as a lithium-specific sorbent.

1. Introduction

Lithium is an element with potentially wide applications in industry; it is used as a useful raw material in such materials as ceramics, medicines and dry batteries and will be utilized in aluminium-based alloys and large-capacity batteries in the near future. In addition, isotopically pure or enriched lithium (^6Li and ^7Li) has applications in nuclear science and industry. For instance, lithium compounds enriched in ^6Li will be required for the tritium breeder blanket in deuterium–tritium fusion power reactors. The total consumption of lithium is thus expected to grow worldwide.

Concurrently with the expected growth in lithium demand, lithium-specific sorbents that have extremely high affinity toward lithium ions have been developed in order to recover lithium from seawater and geothermal water. They include manganese-oxide-based sorbents [1–3], antimonic acids [4, 5] and zirconium-phosphate-based sorbents [6, 7]. If a sorbent shows specific selectivities not only for lithium ions but also for one of the lithium isotopes, it could become an excellent lithium collector and a superb lithium isotope separator simultaneously. Using this sorbent, a process in which lithium isotope separation can be fulfilled when lithium is recovered from seawater could be realized. In this context, we investigated some properties, including selectivity for lithium isotopes, of a lithium-specific sorbent, hereafter designated as $MnO_2(Li)$ and another sorbent, hereafter designated as HMnO(Mg) in previous papers [8, 9]. $MnO_2(Li)$ was prepared by extracting lithium ions from $LiMn_2O_4$ and HMnO(Mg) by extracting magnesium ions from $MgMn_2O_4$.

A sorbent (hereafter designated as HMnO(2Mg)) prepared by extracting magnesium ions from Mg_2MnO_4 is a promising lithium-specific sorbent. It is considered to have the spinel structure belonging to the cubic system [10]. HMnO(2Mg) inherits the same structure that the precursor, Mg_2MnO_4, possesses and lithium ions are regarded as sorbed on the sites that magnesium ions occupied in the precursor [11–13]. In this paper, we report on ion and lithium isotope selectivities of HMnO(2Mg) with various degrees of magnesium extraction.

2. Experimental details

2.1. Preparation of sorbents

The precursor, Mg_2MnO_4, was prepared by heating a mixture of MnOOH and $Mg(OH)_2$ powders with the mole ratio of 1:2 at 900 °C for 4 h in an electric furnace, referring to the method of Miyai *et al.* [12]. Sorbents with different degrees of Mg extraction, DE_{Mg}, i.e. $DE_{Mg} = 32$, 41, 49, 56, 77 and 97%, were prepared by treating Mg_2MnO_4 with 0.5 M (1 M = 1 $mol\,dm^{-3}$) ammonium peroxodisulphate ($(NH_4)_2S_2O_8$) solution under different conditions. Magnesium ions were extracted through the ion exchange with hydrogen ions.

2.2. Ion selectivity

0.1 g of a sorbent 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 containing alkali metal and alkaline earth metal ions at 1.0 mM at 25 °C. After equilibrium was attained between the sorbent and the solution phases,

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*Author to whom correspondence should be addressed.

the sorbent was separated from the solution by filtration. The amount of ion taken up by the sorbent was calculated from the concentration difference before and after the sorption equilibrium. The distribution coefficient, K_d ($\mathrm{cm^3\,g^{-1}}$), of each ion defined as,

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

was then estimated to evaluate the ion selectivity of the sorbent.

2.3. Selectivity for the lithium isotopes

0.1 g of a sorbent was placed in 10.0 $\mathrm{cm^3}$ of a 0.1 M LiOH solution at 25 °C. After equilibrium was attained, the sorbent was separated from the solution by filtration. The sorbent was decomposed with a mixture of 0.1 M HCl and 30% H_2O_2 solutions. Lithium ions in the resultant solution was separated from manganese ions and isolated by cation exchange chromatography, and then, after being converted to lithium iodide, were subjected to mass spectrometry to find out the value of the lithium isotopic ratio, $^7\mathrm{Li}/^6\mathrm{Li}$. Lithium in the solution was also converted to LiI and was subjected to mass spectrometry to determine the $^7\mathrm{Li}/^6\mathrm{Li}$ ratio. The isotopic ratios of lithium in the two phases were measured with the surface ionization technique on a MAT CH-5 mass spectrometer [14]. The ^{7}Li-to-^{6}Li isotopic separation factor, S, defined as,

$$S = (^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{solution}}/(^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{adsorbent}}$$

or

$$\varepsilon = S - 1$$

where $(^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{solution}}$ is the $^7\mathrm{Li}/^6\mathrm{Li}$ isotopic ratio in the solution phase and $(^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{adsorbent}}$ is that in the sorbent phase, was estimated to evaluate the magnitude of the lithium isotope effect caused by the sorbent. The absolute value of the deviation of S from unity, i.e. the magnitude of the ε value, represents the magnitude of the lithium isotope effect. By definition, ε is positive when the lighter isotope, ^{6}Li, is preferentially fractionated into the sorbent phase.

2.4. Other measurements

Other than the measurements of ion and lithium isotope selectivities, we also carried out several measurements such as powder X-ray diffraction, electron spectroscopy for chemical analysis (ESCA) and infrared analysis (IR). The results of such measurements will be shown later as occasion arises.

3. Results and discussion

In Fig. 1, we show the powder X-ray diffraction patterns of five sorbents with different DE_{Mg} values, along with that of the precursor. All the sorbents retain the spinel structure the precursor possessed, although peak intensities reduced with increasing DE_{Mg}. (In passing, the lithium-sorbed sorbent also has a similar X-ray pattern, which shows that the manganese ion–oxide ion framework in HMnO(2Mg) is hardly affected by the existence of lithium ions taken up.) ESCA measurements using MnOOH and MnO_2 as the references for the Mn(III) and Mn(IV) oxidation states, respectively, show that manganese ions in HMnO(2Mg) are all in tetravalent states like those in the precursor. In Table I, we summarize the lattice constants, a_0, of the cubic system calculated from the peak positions at around $2\theta = 18°$ of the X-ray diffraction patterns in Fig. 1. As one can see, the spinel crystal structure shrinks as DE_{Mg} increases, with a relatively large a_0 change between $DE_{\mathrm{Mg}} = 49\%$ and 56%.

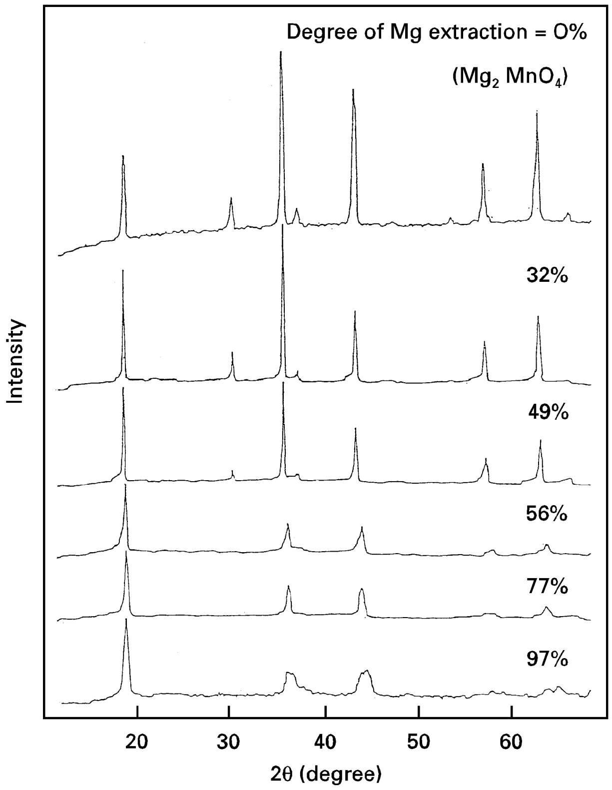

Figure 1 Powder X-ray diffraction patterns of HMnO(2Mg) with varying DE_{Mg} values and Mg_2MnO_4.

TABLE I Lattice constant

Degree of Mg extraction (%)	Lattice constant, a_0 (nm)
0	0.837
32	0.837
49	0.836
56	0.832
77	0.830
97	0.827

In Fig. 2, we depict ion selectivities of HMnO(2Mg) expressed in terms of K_d values as a function of DE_{Mg} at 25 °C. The K_d value for each ion generally increases monotonically with increasing DE_{Mg}, and the high selectivity for the lithium ion reveals itself for sorbents with DE_{Mg} values larger than 50%. The maximum K_d value for the lithium ion achieved at $DE_{\mathrm{Mg}} = 97\%$ is

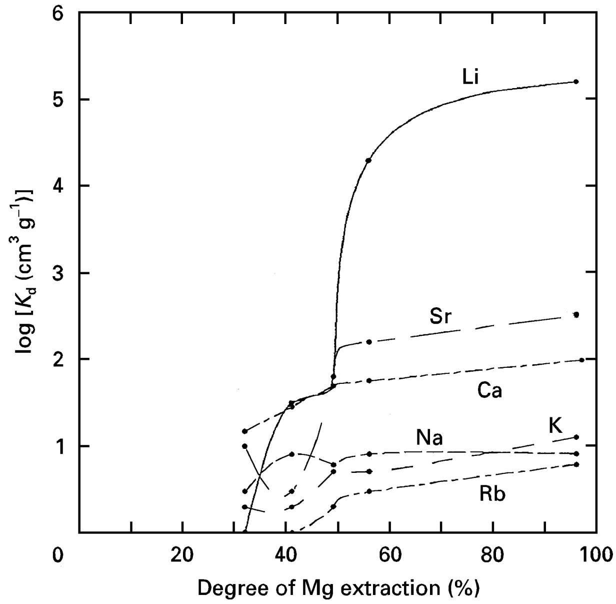

Figure 2 K_ds for alkali and alkaline earth metal ions as functions of DE_{Mg} at 25 °C.

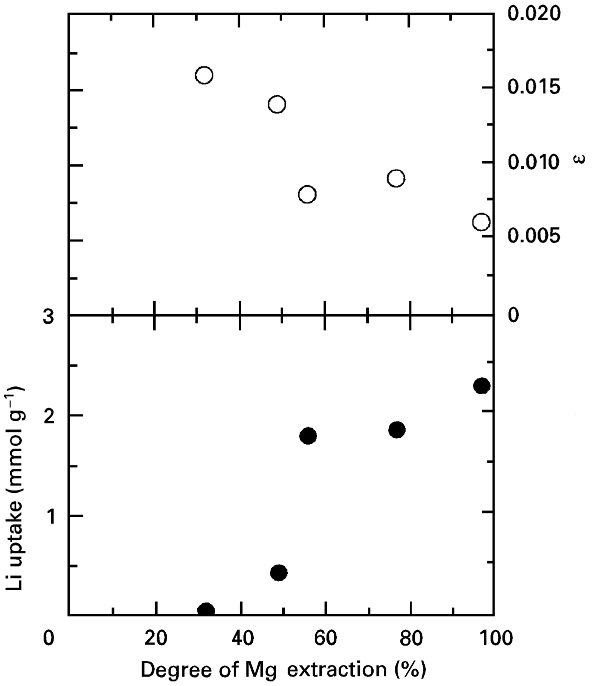

Figure 3 ε (○) and Li uptake (●) as functions of DE_{Mg} at 25 °C.

149 000 cm^3 g^{-1}, which is larger than those observed for MnO_2(Li) [8] and HMnO(Mg) [9].

We show the amount of lithium ions taken up by sorbents from 0.1 M aqueous LiOH solution at 25 °C as a function of DE_{Mg} in the lower half of Fig. 3. Like K_d, it increases monotonically as DE_{Mg} increases, with an abrupt increase between $DE_{Mg} = 49$ and 56%. The maximum Li uptake is 2.26 mmol per 1 g sorbent at $DE_{Mg} = 97\%$. This value is about half the value obtained for MnO_2(Li) and is slightly smaller than that of HMnO(Mg) [8, 9]. Thus HMnO(2Mg), as a lithium-specific sorbent, is superior to MnO_2(Li) and HMnO(Mg) in terms of ion selectivity but it is inferior to them in terms of lithium uptake.

We summarize the lithium isotope effects observed between lithium in the solution phase and lithium sorbed in the sorbents at 25 °C in the upper half of Fig. 3. As one can see, ε is always positive, meaning that HMnO(2Mg) preferentially sorbs ^{6}Li, irrespective of the DE_{Mg} value. This tendency of HMnO(2Mg) in the lithium isotope preference is the same as those of MnO_2(Li) and HMnO(Mg) [8, 9] and of commercially available organic ion exchangers [14]. Like the other properties mentioned above, lithium isotope effects show an abrupt change at $DE_{Mg} = 50\%$; the average ε value is 0.008 for a DE_{Mg} value of more than 50% and 0.015 for a DE_{Mg} value of less than 50%. These ε values should be compared with *c.* 0.002 obtained with organic ion exchangers [14], which are the most intensively investigated for use as packing materials in ion exchange chromatography for lithium isotope separation. Thus, HMnO(2Mg) could be a better lithium isotope separator than organic ion exchangers in terms of the magnitude of lithium isotope effects. However, it shows high lithium isotope selectivity when it does not show high selectivity for lithium nor is its capacity for lithium high. This is a serious drawback as a lithium isotope separator. Thus, at present, HMnO(2Mg) is not a good lithium collector and a good lithium isotope separator simultaneously. However, it may be possible to enhance the lithium isotope effects exhibited by HMnO(2Mg) without losing high selectivity for the lithium ions and moderately high lithium uptake by choosing adequate preparation conditions. We found for MnO_2(Li) that *S* depends more or less on preparation conditions [8] and we may expect a similar dependence of *S* upon preparation conditions for HMnO(2Mg).

The lithium isotope effect found between HMnO(2Mg) and an aqueous solution depends on the difference in the sum of the forces acting on the lithium ions in the two phases [15]. The larger the difference is, the larger the lithium isotope effect becomes. The strengths of the forces are reflected by IR vibrational frequencies of the systems that include lithium ions. Lithium ions are hydrated in the solution phase and captured by oxide ions of the MnO_2 network in HMnO(2Mg). Little is known concerning vibrational data of hydrated lithium ions in aqueous solution. Recently, the totally symmetric stretching frequency of hydrated lithium ions was observed at 192 cm^{-1} [16], which made it possible to give an approximate estimate of the ^{7}Li-to-^{6}Li isotopic reduced partition function ratio [15], $(s/s')f$, the most fundamental quantity in studies on chemical isotope effects, of the hydrated lithium ion. Considering only the first hydration sphere with the hydration number of four, $(s/s')f$ of the hydrated lithium ion in aqueous solution can be estimated by using a simplifying equation for $(s/s')f$ [15],

$$\ln (s/s')f = \Delta M m n (hc\omega/kT)^2/(24MM')$$

where *M* and *M′* are the masses of ^{7}Li and ^{6}Li, respectively, *m* is the mass of a water molecule, *n* is the hydration number, $\Delta M = M - M'$, h is Planck's constant, c is the speed of light, ω is the Li–H_2O totally symmetric stretching frequency, k is Boltzmann constant and T is the absolute temperature. Thus the $(s/s')f$ value of the hydrated lithium ion is calculated as 1.063 at 25 °C. Using this value and the S value above (= 1.015) and applying the isotope distribution theory by Kakihana and Kanzaki [17], the $(s/s')f$ value of the lithium ion sorbed in HMnO(2Mg) is calculated to be 1.048 at 25 °C. When an organic ion exchanger is used as adsorbent, the lithium isotope effect observed is small [14]. This is because lithium ions are hydrated almost equivalently both in the exchanger and solution phases and thus the hydration circumstances of lithium ions are very similar in the two phases [18]. The larger separation factor values obtained here show that the difference in coordination circumstances around lithium ions between HMnO(2Mg) and an aqueous solution is much larger than that between an organic ion exchanger and an aqueous solution.

As shown above, various properties of HMnO(2Mg), as a function of DE_{Mg}, change abruptly at $DE_{\mathrm{Mg}} = 50\%$, and the desirable property as a lithium-specific sorbent reveals itself in HMnO(2Mg) with a DE_{Mg} value larger than 50%. One plausible explanation for this is that there exists a quasi-stable structure of Mg_2MnO_4 when half of the magnesium ions are extracted. A quasi-stable state was reported for half-lithium-extracted $LiMn_2O_4$, the precursor of MnO_2(Li) [19]. We found that the degree of extraction of lithium ions sorbed in MnO_2(Li) depended on the concentration of the extracting agent used [8], while such a phenomenon was not observed for HMnO(2Mg). With 0.01 M HCl, about half of the lithium ions sorbed in MnO_2(Li) were extracted and with 0.05 M or more concentrated HCl almost all the lithium ions were extracted, while lithium ions sorbed in HMnO(2Mg) were extracted even with 0.001 M HCl. These experimental facts seem consistent with the existence of the quasi-stable state of the half-lithium-extracted $LiMn_2O_4$ but not with the existence of the quasi-stable state of half-magnesium-extracted Mg_2MnO_4.

Another possible explanation is that Mg_2MnO_4 has the inverse spinel structure rather than the (normal) spinel structure. Toussaint [10] stated that Mg_2MnO_4 had a spinel structure which was the same as that of Mg_2TiO_4. It is now established that Mg_2TiO_4 has the inverse spinel structure [20]. In the inverse spinel Mg_2MnO_4, magnesium ions occupy half of the octahedral sites surrounded by six oxide ions and tetrahedral sites surrounded by four oxide ions, and manganese ions occupy the remaining half of the octahedral sites. If HMnO(2Mg) is obtained by extracting magnesium ions from Mg_2MnO_4 through the ion exchange with hydrogen ions, it follows that two kinds of absorption sites are formed inside the sorbent and they must show different sorptive properties. The present results are thus consistent with the inverse spinel structure of Mg_2MnO_4, but do not clarify which site plays the more important role for the lithium isotope selectivity of the sorbent.

4. Conclusion

To summarize, we make the following statements concerning the sorbent, HMnO(2Mg), prepared by extracting magnesium ions from Mg_2MnO_4:

1. Various properties of HMnO(2Mg) generally change monotonically as a function of DE_{Mg}, and abrupt changes are observed at $DE_{\mathrm{Mg}} = 50\%$. This seems consistent with the inverse spinel structure of HMnO(2Mg). The characteristics as a lithium-specific sorbent appear for DE_{Mg} values larger than 50%.
2. Isotopically, HMnO(2Mg) is a ^{6}Li-specific sorbent. The maximum ε value was 0.016 at 25 °C. The high lithium isotope selectivity reveals itself when the high lithium ion selectivity does not show up and the lithium uptake is low. Thus at present, HMnO(2Mg) is not an excellent lithium-specific sorbent and a good lithium isotope separator simultaneously.

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