# High Enrichment of Li-6 by Countercurrent Electromigration in Molten $LiNO_3$ with Molten $NH_4NO_3$ at the Cathode

Isao Okada
Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Japan

Kumido Gundo *, Masao Nomura, Yasuhiko Fujii, and Makoto Okamoto
Research Laboratory for Nuclear Reactors, O-okayama, Meguro-ku, Tokyo, Japan

Z. Naturforsch. **41 a**, 1045–1050 (1986); received May 27, 1986

Based on a previously proposed principle, $^6Li$ was enriched from the original abundance 7.4% to 82% with a cell of a new type. Ammonium nitrate melt was used in the relatively large cathode compartment. The enrichment took place around the rather sharp boundary between $LiNO_3$ and $NH_4NO_3$ near the end of a nearly horizontal separation tube opening to the cathode compartment. In 31 days' electromigration no serious corrosion problem was encountered.

## Introduction

If the light isotopes of a metal are to be enriched quickly on a laboratory scale by molten salt countercurrent electromigration, one usually fills the necessarily quite large cathode compartment with an auxiliary salt having the same anions. In order to avoid penetration of the isotopes to be separated into the cathode compartment, the cations of the auxiliary melt must have a greater mobility than the isotopes to be separated. In this way it is possible to have within the separation tube a sharp and stationary boundary between the auxiliary melt and the melt whose cationic isotopes are to be separated. Owing to its position in the separation tube, the portion of the salt with maximum enrichment of the light isotopes is small, and correspondingly its isotope enrichment is large. This principle has for the first time been used in [1] for the enrichment of the light cadmium isotopes.

If the substances produced at the cathode are fluid and compatible with the cell material, such as molten cadmium, thallium and lead or the gases produced in the reaction $NH_4^+ + e^- \rightarrow NH_3 + (1/2)H_2$, they can be withdrawn from time to time or continuously. If they are not compatible with the cell material, such as the alkaline metals, they must be prevented from being produced by admitting the respective gases to the cathode: halogens if the salts are halides or $NO_2 + (1/2)O_2$ if the salts are nitrates.

Lithium ions are the smallest of all univalent cations (besides $H^+$), and therefore for fast enrichment of $^6Li$ an auxiliary salt must be chosen whose mixtures with the lithium salt show the Chemla effect, i.e. a larger mobility of the larger cation. A suitable couple would be the nitrates of lithium and sodium [2]. Contrary to this case, in most cases the Chemla effect exists only in a concentration range from the neat large cation salt up to a critical concentration, where the mobilities of the two cations are equal. If such a couple is chosen, the stationary boundary in the separation column builds up between the auxiliary melt and the critical mixture of the salts, the latter prevailing in the lithium containing part of the separation tube. It is advantageous if the critical mixture contains much of the lithium salt because then much of the isotopically enriched salt will be gained. With increasing temperature the critical concentration increases in lithium content. Also the isotope effect in LiCl [3] and $LiNO_3$ [4, 5] increases with temperature. A suitable couple with deposition of molten thallium in the cathode compartment would be the nitrates of lithium and thallium, the critical concentration at 320 °C being 60 mol% $LiNO_3$ [6] in this case.

The present paper deals with the couple $LiNO_3 + NH_4NO_3$, for which the Chemla effect has been

---

* Present address: Toshiba, Research and Development Center, Komukai, Toshiba-cho 1, Saiwai-ku, Kawasaki, Japan.

Reprint requests to Prof. I. Okada, Department of electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan.

0340-4811 / 86 / 0800-1045 $ 01.30/0. – Please order a reprint rather than making your own copy.

measured in [7]. In this case, because of the difference in melting points ($NH_4NO_3$: mp 170 °C, $LiNO_3$: mp 261 °C) and the ready decomposition of $NH_4NO_3$ at higher temperatures [8] (0.12% in 6 hr at 170 °C, 15% in 40 min at 240 °C [9]), the temperature of the cathode compartment must be lower than that of the separation column, and the boundary between the salts must be kept near the mouth of the separation column, so that the gases into which $NH_4NO_3$ decomposes ($NH_4NO_3 \rightarrow N_2O + 2H_2O$) can escape from the separation tube into the cathode compartment. These, and the gases evolving at the electrodes,

$$\text{Cathode:}\quad NH_4^+ + e^- \rightarrow NH_3 + (1/2)\,H_2$$
$$\text{Anode:}\quad NO_3^- - e^- \rightarrow NO_2 + (1/2)\,O_2\,,$$

could in principle be reunited,

$$NO_2 + 2\,H_2O \rightarrow NH_4NO_3\,,$$
$$NH_3 + (1/2)\,H_2 + NO_2 + (1/2)\,O_2 \rightarrow NH_4NO_3\,,$$

and recycled by filling the product $NH_4NO_3$ into the cathode compartment. A cell of this type (but without recycling), with which $^6$Li was enriched from 7.5% to 90.0% in 38 days, using a separation tube of 25 cm length [10], is described in [11].

The separation tubes of the cells described in the present paper are inclined instead of standing vertically as in [11]. In this way the gases, which in a vertical tube have the tendency to spread over the whole cross section and thus to cut the electric current, collect in the upper part of the cross section and escape into the cathode compartment without disturbing the current.

## Experimental

### *Electromigration cell and procedure*

In the present study, two types of cells (Figs. 1a and 1b), differing from the previous one (Fig. 1c [10, 11]), have been used for two experiments (Exp. 1 and Exp. 2). Data on the cells and experiments are given in Table 1.

Alumina powder was poured into the separation tube through a hole (17 in Fig. 1) and densely packed. Then, quartz wool was cemented to the wall at two places (9 in Figure 1). The cells were wound with a Nichrome tape; the cathode compartment was separately wound with another Nichrome tape so that the temperature of this part could be independently regulated.

Lithium nitrate powder, which had been vacuum-dried at 120 °C overnight, was put into the heated separation tube through the above mentioned hole. After it melted and spread over the diaphragm by capillarity, molten $NH_4NO_3$ was poured into the preheated cathode compartment. Before the molten $NH_4NO_3$ penetrated deeply into the diaphragm part, electromigration was started with a gradually increasing electric current, a long platinum wire dipping into the $NH_4NO_3$ melt being still at a low level. During this initial electromigration for ca. 10 min, more $NH_4NO_3$ melt was added to the planned level, and then the long wire was replaced by a shorter platinum cathode wire of 1 mm ∅. Also the anode was a platinum wire of 1 mm ∅.

The temperature of the cathode compartment was kept at 180 °C with a temperature controller (Model DSM made by Shimaden Electric Co. Ltd., Tokyo). The temperature of the separation tube was not regulated but, the voltage for the electric current passing through the Nichrome heater was stabilized. The fluctuations of the temperature were estimated to be within ± 10 °C. The current was kept constant with a constant DC supplier (Model PAD 500-0.6 made by Kikusui Electric Co. Ltd., Tokyo) during most of the runs (the averaged values are given in Table 1). The current was sometimes adjusted, if necessary, by checking the balance of electromigration and counter flow in the way that will be stated later. The temperature of the molten $LiNO_3$ was measured with a thermocouple inserted into the diaphragm through the hole 17. As the separation tube was heated directly with the Nichrome tape and not dipped in a heat bath, the temperature may have been rather ununiform.

The difference in height between the level of the molten $NH_4NO_3$ in the cathode compartment and the quartz wool of the anode compartment (hydraulic head) was kept at about 23 cm. The level of the melt above the quartz wool (9 in Figure 1a) was not observable. The diameter of the cathode compartment was ca. 2.7 cm. The separation tube inclined by about 10°.

The gases evolving from the anode and the cathode compartments were conducted to a reservoir, where a salt supposed to be $NH_4NO_3$ was produced. Thus no toxic gases were released to the open air.

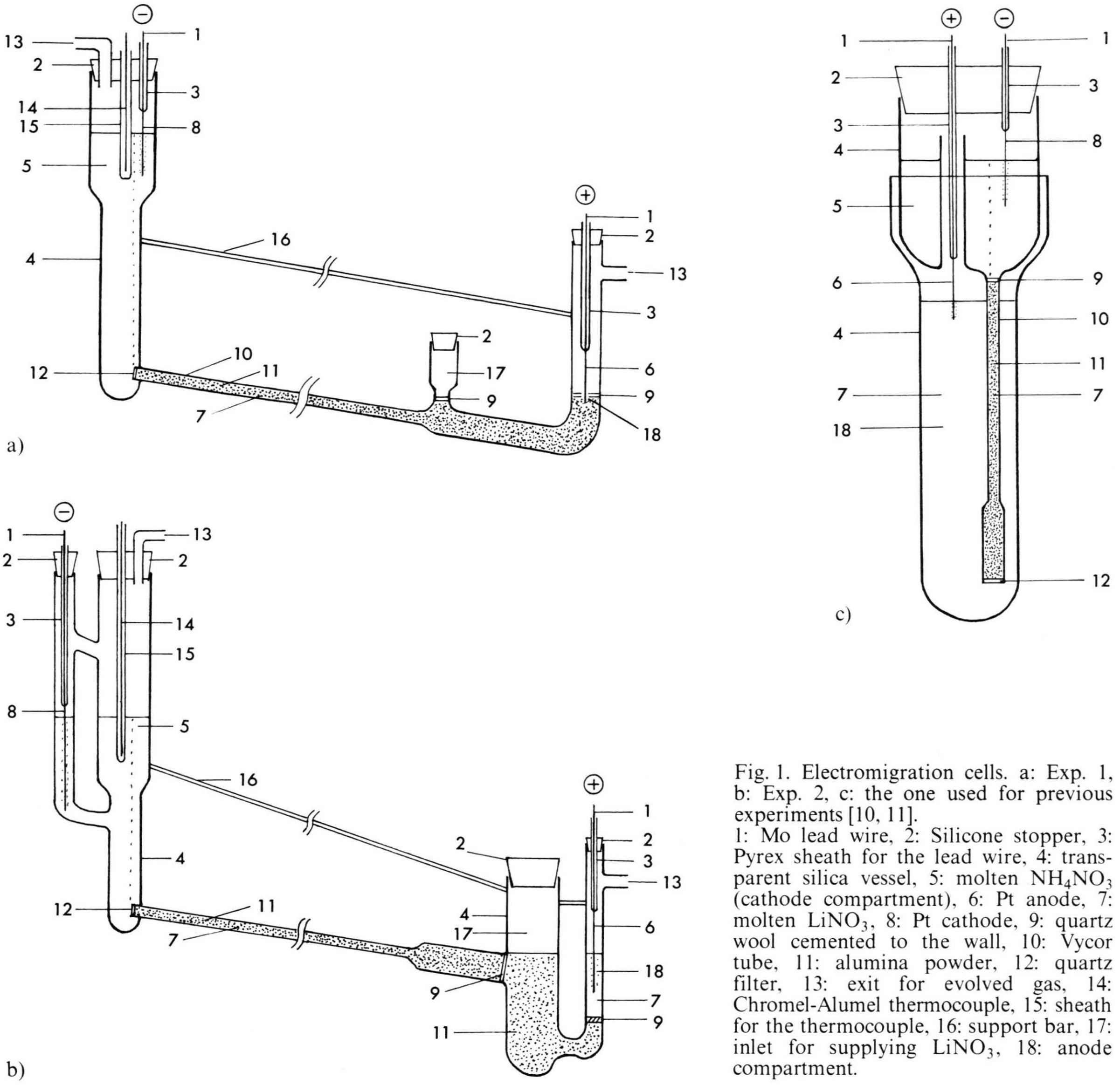

Fig. 1. Electromigration cells. a: Exp. 1, b: Exp. 2, c: the one used for previous experiments [10, 11].
1: Mo lead wire, 2: Silicone stopper, 3: Pyrex sheath for the lead wire, 4: transparent silica vessel, 5: molten $NH_4NO_3$ (cathode compartment), 6: Pt anode, 7: molten $LiNO_3$, 8: Pt cathode, 9: quartz wool cemented to the wall, 10: Vycor tube, 11: alumina powder, 12: quartz filter, 13: exit for evolved gas, 14: Chromel-Alumel thermocouple, 15: sheath for the thermocouple, 16: support bar, 17: inlet for supplying $LiNO_3$, 18: anode compartment.

About 40 g of $NH_4NO_3$ were supplied per day to compensate the expended $NH_4NO_3$ due to the thermal- and electro-decomposition. Small portions of $NH_4NO_3$ (ca. 1 $cm^3$) were sampled for checking the $Li^+$ content at intervals of a few days. If the $Li^+$ content increased, either the electric current had to be reduced or the counter flow had to be increased by adding $NH_4NO_3$ in the cathode compartment.

After the electromigration, all the $NH_4NO_3$ melt in the cathode compartment was taken out and then the cell was cooled by blowing. The separation tube was cut into pieces for chemical analysis and isotope ratio measurement. The quantity of $Li^+$ in each fraction was determined by atomic absorption or ICP (inductively coupled plasma) emission spectroscopy and that of $NH_4^+$ was measured with the Kjeldahl method. The isotope ratio $^7Li/^6Li$ was measured using LiI surface ionization in a Varian MAT CH5 mass spectrometer.

It was inferred from the isotope distribution profile of Exp. 1 that the stationary state was not attained; nevertheless the total amount of $^6Li$ in

Table 1. Electromigration conditions.

| Experimental No. | | 1 | 2 |
|---|---|---|---|
| Electric current | (mA) | 340 | 220 |
| Current density | (A/cm$^2$) | 3.8 | 3.2 |
| Voltage | (V) | 120 − 130 | 260 − 300 |
| Duration | (d) | 21 | 31 |
| Transported charge | (C) | $574 \times 10^3$ | $545 \times 10^3$ |
| Hydraulic head | (cm) | 17 − 23 | 23 − 29 |
| Cell material | | Vycor | Quartz |
| Packing material | | Alumina | Alumina |
| Grain size | (mesh) | ca. 300 | 80 − 100 |
| Temperature | (°C) | | |
| $LiNO_3$ | | ca. 300 | ca. 300 |
| $NH_4NO_3$ | | 180 | 180 |
| Amount of the salt in the cell | | | |
| $LiNO_3$ | (g) | ca. 10 | ca. 145 |
| $NH_4NO_3$ | (g) | ca. 60 | ca. 130 |
| Separation column | | | |
| Length | (mm) | 223 + 128 | 196 + 108 |
| Internal diam. | (mm) | (4) (7) | (4.5) (10.2) |
| Isotope ratio, $^7Li/^6Li$ | | | |
| Original | | 13.89 ± 0.03 | 12.40 ± 0.03 |
| In most enriched fraction (% $^6Li$) | | 0.5038<br>(66.5) | 0.2182<br>(82.1) |
| Overall separation factor between the most enriched fraction and the feed | | 27.6 | 56.8 |

Exp. 1 was insufficient for attaining maximal enrichment. Therefore in Exp. 2 there was a large reservoir from which $^6Li$ was supplied toward the cathode side.

In Exp. 2 the cell was of transparent quartz. There was no detectable difference, however, concerning the cell materials in the two experiments. Alumina powder of a larger grain size (80 − 100 mesh) was used in Exp. 2 in order to make counter flow smoother. At both ends of the reservoir quartz wool was packed and silica-cemented to the cell wall (Aron Ceramic C made by Toagosei Chemical, Nagoya), which prevented the powder in the separation tube and the reservoir from moving.

## Results and Discussion

The distribution of the chemical species and the Li isotopes after electromigration are shown in Figs. 2a and 2b for Exps. 1 and 2, respectively.

The error in the quantity of cations per unit length in the fractions may be mainly due to that in the measurement of the length. In Exp. 2 the $NH_4NO_3$ melt penetrated further into the separation column and the current density was lower than in Exp. 1. A steep concentration gradient of the working salt along the separation tube and a high current density being essential for an efficient isotope fractionation [10], it might have been possible to enrich $^6Li$ to a higher extent during the same period in Exp. 2.

The commercially available $LiNO_3$ used in Exp. 1 happened to be appreciably depleted in $^6Li$, which was often the case several years ago.

In Exp. 1 the amount of Li feed was relatively small and the diameter of the anode part was not so large; therefore, $^7Li$ was considerably enriched at the anode side tailing over an extended region toward the cathode, which is unfavourable for the enrichment of $^6Li$.

In Exp. 1 the cathode compartment after the run contained about 62 g of $NH_4NO_3$ and 0.050 mmol of Li which was considerably enriched in $^6Li$ ($^7Li/^6Li = 1.056$). The amount of $Li^+$ in the cathode compartment varied during the run, which means that the $Li^+$ ions had an appreciable probability of reentering the separation tube and of being further enriched there in $^6Li$ by the high current density.

The total amount of $Li^+$ in Exp. 1 was ca. 0.14 mol according to the chemical analysis, the average isotope ratio of which was 14.2. This is in good agreement with that (13.89) of the original Li, if the errors in the chemical and isotope ratio measurements are taken into account.

In order to learn about the magnitude of the isotope effect of $Li^+$ ions in the boundary region between $NH_4NO_3$ and $LiNO_3$, the elementary separation factor has been determined in mixtures of $LiNO_3$ and $NH_4NO_3$ at relatively low temperature (~ 170 °C). The electromigration cell used for this purpose was similar to that used previously for the determination of the relative difference $\varepsilon_c$ in the internal mobilities, $b$, of $Li^+$ and $NH_4^+$ [7] ($\varepsilon_c = (b_{Li} - b_{NH_4})/\bar{b}$, where $\bar{b}$ is the average cationic internal mobility). The results of 4 experiments (Exps. A, B, C and D) are given in Table 2. Judging from the results of the previous experiments [7], considerable errors are estimated for the $\varepsilon_c$ measurements and consequently for the $\varepsilon_{Li}$ measurements ($\varepsilon_{Li} = (b_6 - b_7)/b_{Li}$, where the suffixes 6 and 7 refer to

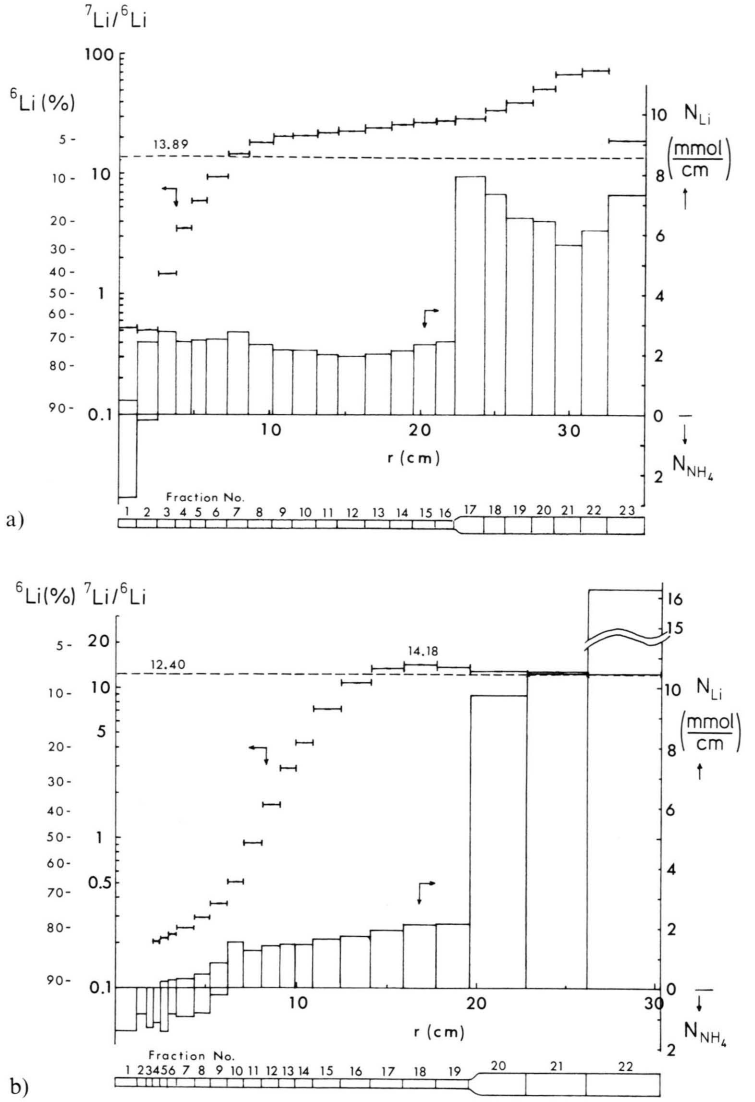

Fig. 2. Distribution of the Li isotopes and the ions $Li^+$ and $NH_4^+$ after the electrolysis. a: Exp. 1, b: Exp. 2. The amounts of $Li^+$ and $NH_4^+$ per cm of tube length are drawn upward and downward, respectively. The abscissa is the distance from the cathode end of the separation tube.

$^6Li^+$ and $^7Li^+$, respectively). If this is taken into account, the concentration dependence of $\varepsilon_{Li}$ is supposed to be small, if any. These $\varepsilon_{Li}$ values are significantly smaller than those determined for pure molten $LiNO_3$ at higher temperature ($\varepsilon_{Li}$ is 0.013 [4] or 0.010 [5] at 300 °C); however, a positive temperature dependence of $\varepsilon_{Li}$ has been observed in pure molten $LiNO_3$, and the extrapolated value to 170 °C is consistent with those observed in the mixtures at 170 °C. The reason for the positive temperature dependence of $\varepsilon_{Li}$ in molten LiCl has been discussed by means of an MD-simulation [12].

In Exp. 2, a distinct enrichment of $^7Li$ was detected around the part of the separation tube where the diameter changes. This is because in the narrow tube the temperature is higher due to Joule heating, and at the higher temperature $\varepsilon_{Li}$ is greater. The region thus acts qualitatively in a similar way as an anode, cf. [13]. In Fraction No. 22, which is adjacent to the quartz wool plug, enrichment of $^7Li$ could not be detected, although this place meets the above condition that two parts with different cross sections are connected. This may be due to the small current density at this place. In Exp. 1 the effect did not

Table 2. Relative difference in the internal mobilities of the two $Li^+$ isotopes, $\varepsilon_{Li}$, in molten $(Li\text{-}NH_4)NO_3$ mixtures.

| Exp. No. | A | B | C | D |
|---|---|---|---|---|
| Temperature (°C) | 170 | 170 | 170 | 170 |
| Transported charge (C) | 8131 | 6859 | 6271 | 2323 |
| Duration (hr) | 48 | 61 | 36 | 14 |
| $x_{Li}$[a] | 0.113 | 0.213 | 0.281 | 0.436 |
| $t_{Li}$[b] | 0.0914 | 0.168 | 0.242 | 0.404 |
| $\varepsilon_c$ | 0.214 | 0.271 | 0.190 | 0.128 |
| $\varepsilon_{Li}$ | 0.0038 | 0.0057 | 0.0058 | 0.0038 |

[a] Initial mole fraction of $LiNO_3$.
[b] Internal transport number of $Li^+$; as for $\varepsilon_c$ and $\varepsilon_{Li}$, see the text.

show up because the $^7Li$ enrichment starting at the anode was tailing there.

In the previous experiments, cells of the type shown in Fig. 1c were employed. The advantages of the cells of the present experiments as compared with the former ones are as follows: (1) The hydraulic head can be more easily adjusted. (2) The amount of $LiNO_3$ is adjustable. (3) A smaller volume of $NH_4NO_3$ can be used. (4) Even if the cathode compartment of the present cells should break by accident, $NH_4NO_3$ will not mix with large amounts of hot $LiNO_3$, while this could happen in the previous cells. Such an accident would be rather dangerous because $NH_4NO_3$ will rapidly thermal-decompose. On the other hand, the disadvantages are as follows. (1) It is more difficult to keep the temperature of the separation tube uniform and to measure it accurately. (2) As the shape is somewhat more complicated, construction of cells is harder. Thus, for the purpose of enrichment only, cells of the present type are more convenient and effective while for measurements of internal mobility differences the former type would be more suitable.

Vycor and quartz were sufficiently resistant against corrosion during the time scale of the present study; however, chemically more resistant materials such as alumina might be preferable for substantially longer runs from the viewpoint of compatibility with $LiNO_3$ melt.

In summary, although the difference in the internal mobilities of the Li isotopes is relatively small in $LiNO_3$, $^6Li$ could be highly enriched without corrosion problems owing to the build-up of a stationary boundary between $LiNO_3$ and $NH_4NO_3$. The present study has revealed the following points for further improvements. (1) It is not so easy to manually set the electric current to its highest possible level and, at the same time, adjust the rate of the counter flow to an appropriate value. If any conventional means for detecting the distribution of $NH_4NO_3$ in a separation tube *in situ* were found, this problem would be solved. (2) An easy method for extracting a small amount of $Li^+$ from $NH_4NO_3$ preferably in the molten state should be found. Suspension of an inorganic ion exchanger selectively extracting $Li^+$ in the cathode compartment may be a possible means for it.

We are indebted to Professor Klemm for helpful suggestions.

The expenses of this work have been defrayed by the Grant in Aid for Scientific Research No. 60470160 from the Ministry of Education, Japan.

[1] A. Klemm, H. Hintenberger, and W. Seelmann-Eggebert, Z. Naturforsch. **3a,** 172 (1948).
[2] C. Yang, R. Takagi, and I. Okada, Z. Naturforsch. **35a,** 1186 (1980).
[3] S. Jordan, R. Lenke, and A. Klemm, Z. Naturforsch. **23a,** 1563 (1968).
[4] L. Lundén and A. Ekhed, Z. Naturforsch. **24a,** 892 (1969).
[5] A. Endoh, I. Okada, M. Nomura, and M. Okamoto, to be published.
[6] K. Kawamura, I. Okada, and O. Odawara, Z. Naturforsch. **30a,** 69 (1975).
[7] I. Okada, T. Ayano, and K. Kawamura, Z. Naturforsch. **37a,** 158 (1982).
[8] A. G. Keenan and B. Dimitriades, Trans. Faraday Soc. **57,** 1019 (1961).
[9] J. D. Brandner, M. Norman, M. Junk, J. W. Lawrence, and J. Robins, J. Chem. Eng. Data **7,** 227 (1962).
[10] I. Okada, K. Ichioka, M. Nomura, K. Kawamura, and H. Kakihana, Asahi Garasu Kogyo Gijitsu Shoreikai Kenkyu Hokoku **32,** 31 (1978) (in Japanese).
[11] I. Okada, Z. Naturforsch. **33a,** 498 (1978).
[12] I. Okada, Z. Naturforsch. **39a,** 880 (1984).
[13] A. Klemm and A. Lundén, Z. Naturforsch. **41a,** 935 (1986).