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

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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the gases produced in the reaction $\text{NH}_4^+ + \text{e}^- \rightarrow \text{NH}_3 + (1/2)\text{H}_2$, they can be withdrawn from time to time or continuously.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 $\text{NO}_2 + (1/2)\text{O}_2$ 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 $\text{LiNO}_3 + \text{NH}_4\text{NO}_3$, for which the Chemla effect has been

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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 ($\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$) can escape from the separation tube into the cathode compartment. These, and the gases evolving at the electrodes,

could in principle be reunited,

and recycled by filling the product NH_4NO_3 into the cathode compartment. A cell of this type (but without recycling), with which ^6Li 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 $\varnothing$. Also the anode was a platinum wire of 1 mm $\varnothing$.

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 $\pm 10^\circ\text{C}$. 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 cm³) 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 $^7\text{Li}/^6\text{Li}$ 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)	574×10^3	545×10^3
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 ₄ NO ₃		180	180
Amount of the salt in the cell			
LiNO ₃	(g)	ca. 10	ca. 145
NH ₄ NO 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, ⁷ Li/ ⁶ Li			
Original		13.89 ± 0.03	12.40 ± 0.03
In most enriched fraction (% ⁶ Li)		0.5038 (66.5)	0.2182 (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 NH₄NO₃ 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 LiNO₃ 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 NH₄NO₃ 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 NH₄NO₃ and LiNO₃, the elementary separation factor has been determined in mixtures of LiNO₃ and NH₄NO₃ 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 ε_c in the internal mobilities, b_i , of Li⁺ and NH₄⁺ [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 ε_c measurements and consequently for the ε_{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.

$^6\text{Li}^+$ and $^7\text{Li}^+$, respectively). If this is taken into account, the concentration dependence of ε_{Li} is supposed to be small, if any. These ε_{Li} values are significantly smaller than those determined for pure molten LiNO_3 at higher temperature (ε_{Li} is 0.013 [4] or 0.010 [5] at 300 °C); however, a positive temperature dependence of ε_{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 ε_{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 ε_{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, ε_{Li} , in molten $(\text{Li-NH}_4)\text{NO}_3$ mixtures.

Exp. No.	A	B	C	D
Temperature ($^{\circ}\text{C}$)	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
ε_{c}	0.214	0.271	0.190	0.128
ε_{Li}	0.0038	0.0057	0.0058	0.0038

^a Initial mole fraction of LiNO_3 .

^b Internal transport number of Li^+ ; as for ε_{c} and ε_{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.

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