High Enrichment of Li-6 by Countercurrent Electromigration in Molten LiNO₃ with Molten NH₄NO₃ 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

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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 LiNO₃ and NH₄NO₃ 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or the gases produced in the reaction \( \text{NH}_4^+ + e^- \rightarrow \text{NH}_3 + (1/2) \text{H}_2 \), they can be withdrawn from time to time or continuously.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 \( \text{H}^+ \)), and therefore for fast enrichment of \( ^6\text{Li} \) 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 LiNO₃ [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% LiNO₃ [6] in this case.

The present paper deals with the couple LiNO₃ + NH₄NO₃, for which the Chemla effect has been

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measured in [7]. In this case, because of the difference in melting points (NH₄NO₃: mp 170 °C, LiNO₃: mp 261 °C) and the ready decomposition of NH₄NO₃ 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 NH₄NO₃ decomposes (NH₄NO₃ → N₂O + 2H₂O) can escape from the separation tube into the cathode compartment. These, and the gases evolving at the electrodes,

\[
\begin{align*}
\text{Cathode:} & \quad \text{NH}_2^+ + e^- \rightarrow \text{NH}_3 + (1/2) \text{H}_2 \\
\text{Anode:} & \quad \text{NO}_3^- - e^- \rightarrow \text{NO}_2 + (1/2) \text{O}_2,
\end{align*}
\]

could in principle be reunited,

\[
\text{NO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4\text{NO}_3,
\]

and recycled by filling the product NH₄NO₃ 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 NH₄NO₃ was poured into the preheated cathode compartment. Before the molten NH₄NO₃ penetrated deeply into the diaphragm part, electromigration was started with a gradually increasing electric current, a long platinum wire dipping into the NH₄NO₃ melt being still at a low level. During this initial electromigration for ca. 10 min, more NH₄NO₃ melt was added to the planned level, and then the long wire was replaced by a shorter platinum cathode wire of 1 mm Ø. Also the anode was a platinum wire of 1 mm Ø.

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 LiNO₃ 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 NH₄NO₃ 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 NH₄NO₃ was produced. Thus no toxic gases were released to the open air.
About 40 g of \(\text{NH}_4\text{NO}_3\) were supplied per day to compensate the expended \(\text{NH}_4\text{NO}_3\) due to the thermal- and electro-decomposition. Small portions of \(\text{NH}_4\text{NO}_3\) (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 \(\text{NH}_4\text{NO}_3\) in the cathode compartment.

After the electromigration, all the \(\text{NH}_4\text{NO}_3\) 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 \(\text{NH}_4\) 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 \(^6\text{Li}\) in
Table 1. Electromigration conditions.

<table>
<thead>
<tr>
<th>Experimental No.</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric current (mA)</td>
<td>340</td>
<td>220</td>
</tr>
<tr>
<td>Current density (A/cm²)</td>
<td>3.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>120−130</td>
<td>260−300</td>
</tr>
<tr>
<td>Duration (d)</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>Transported charge (C)</td>
<td>5.7 x 10⁻⁴</td>
<td>5.45 x 10⁻⁴</td>
</tr>
<tr>
<td>Hydraulic head (cm)</td>
<td>17−23</td>
<td>23−29</td>
</tr>
<tr>
<td>Cell material</td>
<td>Vycor</td>
<td>Quartz</td>
</tr>
<tr>
<td>Packing material</td>
<td>Alumina</td>
<td>Alumina</td>
</tr>
<tr>
<td>Grain size (mesh)</td>
<td>ca. 300</td>
<td>80−100</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>ca. 300</td>
<td>ca. 300</td>
</tr>
<tr>
<td>LiNO₃ (g)</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>NH₄NO₃ (g)</td>
<td>10 ca.</td>
<td>145 ca.</td>
</tr>
<tr>
<td>Separation column Length (mm)</td>
<td>223 + 128</td>
<td>196 + 108</td>
</tr>
<tr>
<td>Internal diam. (mm)</td>
<td>(4) (7)</td>
<td>(4.5) (10.2)</td>
</tr>
</tbody>
</table>
| Isotope ratio, 
Li⁺/⁶Li | Original: 13.89 ± 0.03 12.40 ± 0.03 |
| In most enriched fraction | 0.5038 | 0.2182 |
| (%) ⁶Li | (66.5) | (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 $\varepsilon_c$ in the internal mobilities, $b$, of Li⁺ and NH₄⁺ [7] ($\varepsilon_c = (b_{Li} - b_{NH4})/b$, where $b$ 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...
\(^6\text{Li}^+\) and \(^7\text{Li}^+\), respectively). If this is taken into account, the concentration dependence of \(e_{\text{Li}}\) is supposed to be small, if any. These \(e_{\text{Li}}\) values are significantly smaller than those determined for pure molten LiNO\(_3\) at higher temperature (\(e_{\text{Li}}\) is 0.013 [4] or 0.010 [5] at 300 °C); however, a positive temperature dependence of \(e_{\text{Li}}\) 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 \(e_{\text{Li}}\) in molten LiCl has been discussed by means of an MD-simulation [12].

In Exp. 2, a distinct enrichment of \(^7\text{Li}\) 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 \(e_{\text{Li}}\) 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 \(^7\text{Li}\) 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, \(\varepsilon_{\text{Li}}\), in molten (Li-N\(_4\)H\(_4\))N\(_3\) mixtures.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Transported charge (C)</td>
<td>8131</td>
<td>6859</td>
<td>6271</td>
<td>2323</td>
</tr>
<tr>
<td>Duration (hr)</td>
<td>48</td>
<td>61</td>
<td>36</td>
<td>14</td>
</tr>
<tr>
<td>(x_{\text{Li}})</td>
<td>0.113</td>
<td>0.213</td>
<td>0.281</td>
<td>0.436</td>
</tr>
<tr>
<td>(t_{\text{Li}})</td>
<td>0.0914</td>
<td>0.168</td>
<td>0.242</td>
<td>0.404</td>
</tr>
<tr>
<td>(\varepsilon_{\text{C}})</td>
<td>0.214</td>
<td>0.271</td>
<td>0.190</td>
<td>0.128</td>
</tr>
<tr>
<td>(\varepsilon_{\text{Li}})</td>
<td>0.0038</td>
<td>0.0057</td>
<td>0.0058</td>
<td>0.0038</td>
</tr>
</tbody>
</table>

* Initial mole fraction of LiN\(_3\).
\(b\) Internal transport number of Li\(^+\); as for \(\varepsilon_{\text{C}}\) and \(\varepsilon_{\text{Li}}\), see the text.

... show up because the \(^7\)Li 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 LiN\(_3\) is adjustable. (3) A smaller volume of NH\(_4\)N\(_3\) can be used. (4) Even if the cathode compartment of the present cells should break by accident, NH\(_4\)N\(_3\) will not mix with large amounts of hot LiN\(_3\), while this could happen in the previous cells. Such an accident would be rather dangerous because NH\(_4\)N\(_3\) 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 LiN\(_3\) melt.

In summary, although the difference in the internal mobilities of the Li isotopes is relatively small in LiN\(_3\), \(^6\)Li could be highly enriched without corrosion problems owing to the build-up of a stationary boundary between LiN\(_3\) and NH\(_4\)N\(_3\). 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\(_4\)N\(_3\) 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\(_4\)N\(_3\) 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.

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