Lithium Isotope Effect Accompanying Electrochemical Insertion of Lithium into Liquid Gallium

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Lithium was electrochemically inserted from a 1 : 2 (v/v) mixed solution of ethylene carbonate (EC) and methylethyl carbonate (MEC) containing 1 M LiClO4 into liquid gallium to observe lithium isotope effects accompanying the insertion. It was observed that the lighter isotope 6Li was preferentially fractionated into liquid gallium with the single-stage lithium isotope separation factors S, ranging from 1.005 to 1.031 at 50 °C and 1.003 to 1.024 at 25 °C. The lithium isotope effects estimated by molecular orbital calculations at the B3LYP/6-311G(d) level of theory agreed qualitatively with those of the experiments, but the quantitative agreement of the two was not satisfactory.

Key words: Lithium Isotope Effects; Electrochemical Insertion; Gallium; Molecular Orbital Calculation; Reduced Partition Function Ratio.

1. Introduction

Lithium isotopes play important roles in the nuclear industry. A large demand for the lighter isotope of lithium, 6Li, is expected in deuterium tritium (DT) fusion power reactors in the future, where lithium compounds rich in 6Li will be required for the tritium breeder blanket. The heavier isotope of lithium, 7Li, is used as corrosion inhibitor of coolants in nuclear fission reactors. These are examples showing the importance of the isolated and/or enriched isotopes of lithium.

The only method until now that was applied to a large-scale lithium isotope separation is the amalgam method [1], in which lithium is distributed between the amalgam phase and the aqueous or organic electrolyte solution phase. This lithium isotope separation is based on the lithium isotope exchange reaction between the two phases

\[ {^7}\text{Li}(\text{Hg}) + {^6}\text{Li}^+(\text{SOL}) \rightleftharpoons {^6}\text{Li}(\text{Hg}) + {^7}\text{Li}^+(\text{SOL}), \]  

where A Li(Hg) and A Li+(SOL) denote the isotope A surrounded by mercury atoms in the amalgam phase and the solvent molecules in the electrolyte solution phase, respectively. The 7Li-to-6Li single-stage separation factor S, defined as

\[ S = (\frac{{^7}\text{Li}/^{6}\text{Li}}_{\text{sol}})/(\frac{{^7}\text{Li}/^{6}\text{Li}}_{\text{Hg}}), \]  

where \( (\frac{{^7}\text{Li}/^{6}\text{Li}}_{\text{sol}}) \) and \( (\frac{{^7}\text{Li}/^{6}\text{Li}}_{\text{Hg}}) \) denote the 7Li/6Li isotopic ratios in the solution and amalgam phases, respectively, is reported to be 1.049 to 1.062 [2], meaning that 6Li is preferentially fractionated in the amalgam phase. The reaction (1) is a redox reaction between the neutral lithium atom and the monovalent lithium ion. Large isotopic effects observed in the amalgam method seem mainly to come from the valence change of lithium accompanying the redox reaction.

Although large lithium isotopic effects are attractive, the use of toxic mercury makes the amalgam method difficult to be applied to large-scale lithium isotope enrichment in the future. Thus, it seems important to seek for material that is not or less toxic and can take up lithium utilizing the redox reaction. In this context, we investigated tin [3], graphite [4], metal oxides [5], zinc [6], and tin sulfide [7] as a possible alternative to mercury and found that tin, graphite, zinc, and tin sulfide preferentially take up 6Li, while metal oxides show little preference or are slightly 7Li-specific. Unfortunately, the S values on these materials could not surpass those on mercury.
Gallium could be an alternative to mercury. It can be in the liquid state at ambient temperature (the melting point is 29.8 °C). This property of gallium is similar to that of mercury. We have investigated isotopic effects accompanying electrochemical lithium insertion into solid gallium and reported that it preferentially takes up $^6$Li [8]. The $S$ values on solid gallium ranged from 1.015 to 1.025.

In this paper, we report lithium isotopic effects accompanying electrochemical insertion of lithium into liquid gallium and the results of molecular orbital (MO) calculations of lithium species related to these processes.

2. Experimental and Calculations

2.1. Reagents

Gallium with a purity of 99.9999% used as host material for the lithium insertion was from Dowa Mining Co. Ltd. In some experiments, gallium was treated with 2 M HCl acetone solution for removing gallium oxide formed on the surface before used. More specifically, 0.3 cm$^3$ of liquid gallium was immersed in a HCl acetone solution for 30 minutes with stirring, and this treatment was repeated twice. Lithium foils, 1 mm thick and with a purity of 99.8% used as anodes and reference electrodes, were purchased from Honjo Metals Co. Ltd. A 1 : 2 v/v mixed solution of ethylene carbonate (EC) and methylethyl carbonate (MEC) containing 1 M LiClO$_4$ (LIPASTE-E2MEC/1), used as an organic electrolyte solution, was purchased from Tomiyama Pure Chemical Ind. Ltd. The other reagents were of reagent grade and used without further purification except for hexane, which was used after dehydration with molecular sieves.

2.2. Electrochemical Insertion of Lithium into Liquid Gallium

The experimental apparatus used is schematically drawn in Figure 1. It includes a power supply (a Hokuto Denko Corporation HJ-201B battery charge/discharge unit), a three-electrode electrochemical cell (electrolytic cell), and a data acquisition unit consisting of an A/D converter and a personal computer. The electrolytic cell was build up in a dry argon atmosphere. Lithium foils of about 7 mm $\times$ 7 mm size, attached to stainless meshes by pressing, were used as anode and reference electrode. The weight of liquid gallium working as cathode was 5 to 12 g. The surface area of the liquid gallium cathode contacting the electrolyte was about 0.78 cm$^2$. A platinum wire connecting the gallium electrode and the outer wiring system was coated by a Teflon tube to prevent the wire contacting the electrolyte solution. The volume of the electrolyte solution placed in was 7 to 11 cm$^3$.

The lithium insertion (electrolysis) was performed in a constant-current constant-voltage mode without stirring the liquid gallium cathode since stirring led to the formation of a gallium-electrolyte emulsion. The electrolysis was at first carried out in a constant current mode (3 mA). As it proceeded, the electric potential of the cathode against the lithium reference electrode (cathode potential) was gradually decreased and reached the predetermined value set at 0.02 V. The electrolytic mode was then automatically changed to the constant voltage mode; the electrolysis was continued and the electric current gradually decreased while keeping the cathode potential constant at the predetermined value. As the lithium insertion proceeded, the formation of a gallium-lithium alloy film on the surface of the liquid gallium cathode was observed. Analyses of the amount of inserted lithium and lithium isotope ratios were conducted with this alloy film. The electrolysis continued until the integrated quantity of electricity reached the predetermined value and was discontinued manually. During the electrolysis, the temperature of the electrolytic cell was kept constant (25 or 50 °C).

2.3. Analyses

After the electrolysis was finished, the gallium-lithium alloy film formed on the surface of liquid gallium cathode was taken out of the cell, washed with
dehydrated hexane, and allowed to stand for a day to remove adhering hexane by evaporation. The lithium extraction and the isolation from the gallium-lithium alloy and the sample preparation for the mass spectrometric analysis for the $^{7}\text{Li}/^{6}\text{Li}$ isotopic ratio were carried out as follows. The gallium-lithium alloy was first dissolved with 12 M HCl solution and thereafter, the HCl concentration of the resultant solution was adjusted to 4 M. Lithium in this solution was separated from gallium by solvent extraction using tributyl phosphate as the organic phase with 1:1 volume ratio of the aqueous and the organic phases. In the solvent extraction, gallium was extracted into the organic phase, while lithium remained in the aqueous phase. The amount of lithium in the gallium-lithium alloy was determined by measuring the lithium concentration in the aqueous phase with a Thermo Electron Corp. SOLAAR M mkII atomic absorption spectrometer.

For the lithium isotopic analysis, the chemical form of lithium in the aqueous phase was converted to lithium iodide through cation and anion exchanges and addition of HI. An aliquot of the electrolyte solution, after the lithium insertion, was also subjected to cation and anion exchanges for purification. The purified lithium was finally converted to iodide. Using the purified lithium (lithium iodide) in this way, the $^{7}\text{Li}/^{6}\text{Li}$ isotopic ratios of the gallium-lithium alloy and the organic electrolyte solution were determined to estimate $S$, accompanying the lithium insertion, defined as

$$S = \left( \frac{^{7}\text{Li}/^{6}\text{Li}_{\text{sol}}}{^{7}\text{Li}/^{6}\text{Li}_{\text{Ga}}} \right),$$  \hspace{1cm} (3)

where $^{7}\text{Li}/^{6}\text{Li}_{\text{sol}}$ and $^{7}\text{Li}/^{6}\text{Li}_{\text{Ga}}$ are the lithium isotopic ratios of the electrolyte solution and the gallium-lithium alloy, respectively. By definition, $S$ should be larger than unity when $^{6}\text{Li}$ is preferentially taken up by gallium. The $^{7}\text{Li}/^{6}\text{Li}$ ratios of the samples were determined by the surface ionization technique with a Finnigan MAT261 mass spectrometer. The procedure of the lithium isotopic measurements are described in [9].

2.4. Molecular Orbital (MO) Calculations

MO calculations were performed to discuss the lithium isotope effects observed in the present study. Clusters in which lithium atoms were bonded to a gallium atom, Li$_{n}$Ga ($n = 1 - 8$), were employed as model systems for the gallium-lithium alloy; the number of lithium atoms was expected to be larger than that of gallium in the area of the gallium cathode, where lithium was taken up from the electrolyte solution. A lithium ion solvated by ethylene carbonate (EC) molecules, Li$^+$(EC)$_{n}$ ($n = 1 - 6, 8$), was employed as model species in the electrolyte solution. We have already reported [10] that EC molecules are preferentially solvated to a lithium ion in the EC/MEC mixed solvent system and the number of EC molecules in the primary salvation sphere is four. The structures of those models were first optimized, and then frequencies were calculated at respective optimized structures. Reduced partition function ratios (RPFRs), that means $(s/s')f$ (see (4)) were determined using the calculated frequencies:

$$\frac{(s/s')f}{\prod_{i=1}^{f} u_i \exp(-u_i/2)/\{1 - \exp(-u_i)\}} \left(1 - \frac{(s/s')f}{\prod_{i=1}^{f'} u_i' \exp(-u_i'/2)/\{1 - \exp(-u_i')\}} \right),$$  \hspace{1cm} (4)

where $u_i = h\omega_i/(kT)$ and $u_i' = h\omega_i'/(kT)$; $f$ is the degree of freedom of molecular vibration, $h$ is the Planck constant, $c$ is the velocity of light, $\omega_i$ and $\omega_i'$ are the wavenumbers of the $i$th molecular vibration of the heavier and the lighter isotopic species, respectively, $k$ is the Boltzmann constant, and $T$ is the absolute temperature.

All the calculations were made at the B3LYP/6-311G(d) level of theory using the Gaussian 98 and 03 program packages [11]. The Gauss View program (Gaussian Inc.) and the Free Wheel program (Butch Software Studio) were used for the graphics.

No symmetry consideration was made in the geometry optimization calculations: For each of the structures considered, bond lengths, bond angles, and dihedral angles were varied independently to achieve the geometric optimization. Only the mono isotope substitutions were considered for all possible combinations of isotopic species.

3. Results and Discussion

3.1. Results of the Electrochemical Insertion of Lithium into Liquid Gallium

Experimental conditions and results are summarized in Table 1. The lithium insertion time and the amount of inserted lithium ranged from 6.4 to 9.4 hours and from 0.15 to 0.78 mmol, respectively. The electric current efficiency, defined as 100 times the amount of inserted lithium determined by flame photometry divided by the integrated quantity of electricity, was from 42 to 95%. The experimental temperature was 50 °C in
Table 1 lists the $S$ values obtained in the present work. They are all larger than unity, ranging from 1.003 to 1.031. This means the lighter isotope $^6$Li was preferentially fractionated into the liquid gallium phase in every experiment. This tendency of lithium isotope fractionation is the same as that observed using solid gallium as a cathode [8].

The lithium isotope fractionation observed in the present experiments is considered to be based on the isotope exchange equilibrium between the gallium-
lithium alloy phase and the electrolyte phase:

\[
^7\text{Li}(\text{Ga}) + ^6\text{Li}^+(\text{SOL}) = ^6\text{Li}(\text{Ga}) + ^7\text{Li}^+(\text{SOL}),
\]

where \(^A\text{Li}(\text{Ga})\) and \(^A\text{Li}^+(\text{SOL})\) denote the lithium isotopotope \(A\) in the gallium-lithium alloy and the electrolyte phases, respectively. If the isotope exchange equilibrium in (6) was established during the lithium insertion into liquid gallium, the obtained \(S\) value is equal to the equilibrium constant \(K\) of (6) and the deviation from unity, \(\varepsilon = K - 1\), shows the magnitude of lithium isotope effects. According to the theory of equilibrium isotope effects based on molecular vibrations [14], the observed isotope effects come from the difference in the sum of forces acting on lithium in the liquid gallium and the electrolyte phases. The preferential fractionation of \(^6\text{Li}\) into the alloy phase means that the magnitude of that sum was larger in the electrolyte than in the alloy.

The obtained \(S\) values in Runs A1–A9, where the electrolysis was performed at 50 °C, ranged from 1.005 to 1.031 with the average of 1.017, while in Runs B1–B4, performed at 25 °C, the \(S\) values ranged from 1.003 to 1.016 with the average of 1.010. Thus, although it is theoretically predicted that the magnitude of equilibrium isotope effects is inversely proportional to the square of the absolute temperature \(T\) [14], the temperature dependence of the lithium isotope effects did not obey this rule in the present study.

The gallium oxide film formed on the surface of liquid gallium was not removed in advance of electrolysis in Runs A9 and B1–B4. We had considered if a part of the gallium cathode surface had been oxidized to gallium oxide, the magnitude of the isotope effect would decrease because of the expected strong interaction between oxygen atoms of the oxide and an inserted lithium atom [5]. Against our speculation, the \(S\) value of Run A9 carried out without the removal of the gallium oxide was 1.024, that means larger than 1.016, the average value of \(S\) of Runs A1–A8 in which the oxide film had been removed in advance. Furthermore, the \(S\) values in Runs B1–B4, 1.003 to 1.016, were smaller than that in Run A9. Thus, we can not draw a conclusion that the effect of removal of gallium oxide film contribute to enhance the \(S\) value.

There were no clear correlations between the \(S\) value and other experimental conditions such as the insertion time, the amount of inserted lithium or the current efficiency. To summarize the results on the observed lithium isotope effect, it is quite certain that the lighter isotope, \(^6\text{Li}\), was preferentially fractionated into the liquid gallium, its magnitude had no clear correlation with experimental factors within the range of the present experimental conditions. One of probable reasons for this may be the lack of stability at the electrolyte-electrode interface during the formation of the gallium-lithium alloy described in Section 3.1 above. This lack of stability may affect the results of experimental measurements including the values of \(S\).

In our previous work [8] in which solid gallium was used as the host material of lithium insertion, the obtained \(S\) value ranged from 1.015 to 1.025 with the average of 1.021. The large scattering of \(S\) data was not seen there unlike the present experiments. In the case of solid gallium, the gallium-lithium alloy is formed on the solid gallium surface and the solid-liquid mixed state does not exit, which may lead to the condition that the isotope exchange equilibrium can be better established during the lithium insertion. It seems such a condition made it possible to obtain experimental results with small data scattering.

### 3.3. Molecular Orbital (MO) Calculations

The stabilization energies and the RPFRs of Li(EC)\(n\) (\(n = 1–6, 8\)) and Li\(_x\)Ga (\(n = 1–8\)) are summarized in Table 2. The RPFR values of gallium-lithium clusters are the averages of the RPFR values calculated for the

| Table 2. Stabilization energies and RPFRs for solvated lithium ions and gallium-lithium clusters. |
|---|---|---|
| \(n\) Species\(^a\) | Stabilization energy \((\text{kJmol}^{-1})\) | RPFR \((\text{SOL})\) |
| Gallium-lithium cluster | | |
| 1 | Ga-Li | −0.5 | 1.01941 |
| 2 | Ga-(Li)\(_2\) | −1.2 | 1.01516 |
| 3 | Ga-(Li)\(_3\) | −1.9 | 1.01712 |
| 4 | Ga-(Li)\(_4\) | −2.5 | 1.02029 |
| 5 | Ga-(Li)\(_5\) | −3.2 | 1.02236 |
| 6 | Ga-(Li)\(_6\) | −3.8 | 1.02119 |
| 7 | Ga-(Li)\(_7\) | −4.5 | 1.01972 |
| 8 | Ga-(Li)\(_8\) | −5.0 | 1.01979 |

\(\text{SOL}\), \(\text{RPFR}\), \(\text{Li}^+\), \(\text{Ga}^\text{III}\), \(\text{EC}\) denote the lithium isotope effect, the lighter isotope, \(^6\text{Li}\), was preferentially fractionated into the liquid gallium, its magnitude had no clear correlation with experimental factors within the range of the present experimental conditions. One of probable reasons for this may be the lack of stability at the electrolyte-electrode interface during the formation of the gallium-lithium alloy described in Section 3.1 above. This lack of stability may affect the results of experimental measurements including the values of \(S\).
mono isotope substitutions. Examples of the optimized structures are depicted in Figures 2 and 3 showing the structure of Li(EC)$_4$, Li(EC)$_6$, Li$_5$Ga, and Li$_8$Ga.

In Li(EC)$_n$ ($n = 1 – 6, 8$), the EC molecules in the primary salvation sphere, where the salvation number was four as before [10], were bonded to the central Li$^+$ ion using their carbonyl oxygen atoms. Even if we tried to make more than four EC molecules to be solvated to the Li$^+$ ion, only four EC molecules were directly bonded to the Li$^+$ ion and the others moved to the secondary salvation sphere at the optimized structures. The result for the stabilization energies is that the largest stability was obtained for Li$^+(EC)_4$, support this conclusion.

For Li$_n$Ga, lithium atoms were bonded to the hemisphere of the gallium atom for $n$ up to 5, while for $n = 6$ and 8, the gallium atom tended to be located at the central position of the clusters. The stabilization energy for optimized structures increased with increasing $n$.

The isotope exchange equilibrium constant $K$ for (6) can be estimated using the values of the RPFRs at the optimized structures:

$$K = \frac{f_{Li^+(SOL)}}{f_{Li(Ga)}},$$

(7)

where $f_{Li^+(SOL)}$ and $f_{Li(Ga)}$ represent the RPFR value of solvated lithium ion and the gallium-lithium cluster, respectively. As the RPFR value of the solvated lithium ion we use 1.08491 of Li$^+(EC)_4$ that has the largest stabilization energy among the Li(EC)$_n$ ($n = 1 – 6, 8$) considered. The calculated RPFR value of the gallium-lithium cluster seems to be independent of the stabilization energy of the cluster. So, we use 1.01949, the average of the RPFRs of all optimized structures, as the RPFR of lithium in the gallium-lithium alloy. With these RPFR values we calculated $K$ to 1.06417 at 25 $^\circ$C (and 1.05326 at 50 $^\circ$C). Calculations thus agree with the experiments qualitatively in that the heavier lithium isotope should be enriched in the solution phase. However, they do not agree quantitatively. In the present experiments, the obtained separation factors ranged from 1.005 to 1.031 with the largest obtained in Run A3. The maximum value of the experimental $\varepsilon(S – 1)$ is thus 0.031, much smaller than the value of 0.053 estimated by MO calculations. This discrepancy may indicate the possibility that the isotope exchange equilibrium was not established during the lithium insertion.

3.4. Comparison with the Amalgam Method

One of the expectations of the present study is to observe large lithium isotope effects comparable with those in the amalgam method with liquid mercury. The obtained $S$ values, however, were 1.003 to 1.031, much smaller than 1.049 to 1.062 of the amalgam method.
A reason for the large difference in lithium isotope effects between the two methods may be the smallness of the RPFR value of lithium in the amalgam phase. We have reported MO calculations at UB3LYP/LanL2DZ level for diatomic lithium compounds [15]. The results showed that the RPFR value of Hg-Li, 1.0013, is smaller than that of Ga-Li, 1.0110, which means that the $K$ value of (1) is expected to be larger than that of (6) if the lithium species in the electrolyte phase is the same.

Another plausible reason is the difference in the state of lithium in the amalgam and the gallium-lithium alloy phases. A lithium atom in the amalgam phase may exist as a mercury-lithium complex and does not form a solid alloy film like the gallium-lithium alloy. The interface between the mercury phase and the electrolyte phase must be stable and the isotope exchange equilibrium can be established. The experimental $S$ values obtained in the amalgam method are thus close to those estimated computationally.

4. Conclusion

To summarize, we make the following statements:

1. Lithium was electrochemically inserted from a 1:2 (v/v) mixed solution of ethylene carbonate (EC) and methyl ethyl carbonate (MEC) containing 1 M LiClO$_4$ into liquid gallium. The formation of a gallium-lithium alloy film on the surface of the liquid gallium cathode was observed during the insertion of lithium. Lithium isotope effects accompanying the insertion were observed. The lighter isotope was preferentially fractionated into liquid gallium, which indicated that the sum of forces acting on lithium in an electrolyte solution is larger than that in liquid gallium. The obtained single-stage lithium isotope separation factor $S$ ranged from 1.005 to 1.031 at 50 °C and from 1.003 to 1.024 at 25 °C, independent of the experimental conditions.

2. Molecular orbital calculations of solvated lithium ions and gallium-lithium clusters, which were models of lithium species in the electrolyte phase and the gallium-lithium alloy, respectively, were performed to analyze the observed lithium isotope effects. The structures of the models were optimized at the B3LYP/6-311G(d) level of theory and their $^6$Li-to-$^7$Li isotopic reduced partition function ratios (RPFRs) were estimated. The lithium isotope exchange equilibrium constant $K$ at 25 °C calculated by the RPFR values for the models was 1.064, which is much larger than the observed $S$ values, 1.005 to 1.031. This large discrepancy indicates the possibility that the isotope exchange equilibrium was not fully established during the lithium insertion.

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