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Lithium isotope effect accompanying electrochemical insertion of lithium into gallium

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Abstract

Lithium has been electrochemically inserted from a 1:2 (v/v) mixed solution of ethylene carbonate (EC) and methylethyl carbonate (MEC) containing 1 M $LiClO_4$ or from dimethyl sulfoxide (DMSO) containing 1 M LiCl into gallium, and the lithium isotope fractionation accompanying the insertion has been observed. The lighter isotope was preferentially fractionated into gallium, which was in accordance with the theory of the equilibrium isotope fractionation arising from molecular vibrational quantum effects. The single-stage lithium isotope separation factor ranged from 1.015 to 1.025 at 25 °C. It was independent both of the kind of electrolyte solution and of the chemical composition of the Li–Ga alloys formed within the experimental range studied and within experimental uncertainty.

Keywords: Lithium isotope; Gallium; Separation factor; Isotope fractionation; Redox; Electrochemical insertion

1. Introduction

Lithium has been and still is a main target of isotope separation study. This is because, in part, of the importance of the isolated and enriched isotopes of lithium in nuclear science and industry. The heavier isotope of lithium, ^{7}Li, is used as pH controller of coolants in nuclear fission reactors due to its small thermal neutron absorption cross section. A large demand for the lighter isotope, ^{6}Li, is expected in DT fusion power reactors in the future where lithium compounds rich in ^{6}Li will be required for the tritium breeder blanket. It may also be used as control material in RAPID (Refueling by all pins integrated design) reactors (Kambe, 2004).

The only method that was applied to a large-scale lithium isotope separation is the so called amalgam method (Palko et al., 1976). In this method, lithium is distributed between the amalgam phase and the aqueous or organic electrolyte solution phase and lithium isotope separation is practiced based on the lithium isotope exchange reaction between the two phases

$$^7\mathrm{Li}_{\mathrm{Hg}} + {}^6\mathrm{Li}^+_{\mathrm{sol}} = {}^6\mathrm{Li}_{\mathrm{Hg}} + {}^7\mathrm{Li}^+_{\mathrm{sol}}, \qquad (1)$$

where $^A\mathrm{Li}_{\mathrm{Hg}}$ and $^A\mathrm{Li}^+_{\mathrm{sol}}$ denote the isotope A surrounded by mercury atoms in the amalgam phase and solvent molecules in the electrolyte phase, respectively. The reported value of the ^{7}Li-to-^{6}Li single-stage separation factor, *S*, defined as

$$S = (^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{sol}}/(^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{Hg}}, \qquad (2)$$

where $(^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{sol}}$ and $(^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{Hg}}$ denote the ^{7}Li/^{6}Li isotopic ratios in the solution and amalgam phases, respectively, is 1.049–1.062 for the water solvent (Fujie et al., 1986), meaning that ^{6}Li is preferentially fractionated in the amalgam phase. Although the value of 1.049–1.062 is large and attractive, the use of toxic mercury brings about biological and environmental problems and makes the amalgam method difficult to be applied to large-scale lithium isotope enrichment in the future.

The reaction of Eq. (1) is in principle a redox reaction between the neutral lithium atom and the monovalent lithium ion. There may be some non- or less-toxic material that can be a medium for the redox reaction of lithium. As a possible alternative of mercury, we investigated tin (Yanase et al., 2000), graphite (Yanase et al., 2003) and metal oxides (Mouri et al.,

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2007). We found that tin and graphite preferentially took up ^{6}Li, while metal oxides showed little preference or were slightly ^{7}Li-specific. Unfortunately, the *S* values on these materials could not surpass those on mercury.

Gallium is another candidate of the substitute for mercury. The existence of lithium–gallium alloys up to the composition Li_2Ga is known at room temperature and charge-discharge study on a LiGa/Li cell was reported (Saint et al., 2005). In this paper, we report lithium isotope effects accompanying electrochemical insertion of lithium into solid gallium.

2. Experimental

2.1. Reagents

Gallium with a purity of 99.9999% used as the host material of the lithium insertion was purchased from Dowa Mining Co. Ltd. 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. Dimethyl sulfoxide (DMSO) was a product of Wako Pure Chemical Ind. Ltd. DMSO containing 1 M lithium chloride was used as another electrolyte solution. 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 gallium

The experimental apparatus used is basically the same as the one used in the previous study (Yanase et al., 2003) and schematically drawn in Fig. 1. It was composed of 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. Lithium foils of about 7 mm × 7 mm size, attached to stainless meshes by pressing, were used as anode and reference electrode. A gallium cathode (a gallium foil) of about 20 mm × 5 mm × 0.025 mm size was made by pouring fused gallium into a mold. The electrolytic cell was built up in a dry argon atmosphere as shown in Fig. 1. The volume of the used electrolyte solution was 7–11 cm^3 and the cathode was placed so that the gallium foil was wholly immersed in the electrolyte solution.

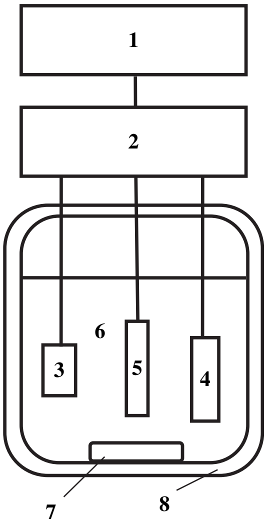

Fig. 1. The experimental apparatus. 1, data acquisition unit; 2, power supply; 3, lithium reference electrode; 4, lithium anode; 5, gallium cathode; 6, electrolyte solution; 7, stirrer tip; 8, electrolytic cell.

The lithium insertion was performed in a constant current–constant voltage mode, that is, the electrolysis (lithium insertion) was at first carried out in a constant current mode (3 mA). As the electrolysis proceeded, the electric potential of the cathode against the lithium reference electrode (cathode potential) 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 is continued and the electric current gradually decreases while keeping the cathode potential constant at the predetermined value. It should be noted, however, that, in the majority of the experiments with the EC/EMC mixed solvent, no appreciable voltage drop was observed in the constant current mode, and consequently, no mode change in electrolysis actually occurred. 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 at 25 °C and the electrolyte solution was stirred by a magnetic stirrer.

In many experiments, we observed that part of the gallium cathode peeled off the rest into the electrolyte solution during the electrolysis, which indicated that the electrode became fragile by the lithium insertion and the formation of lithium–gallium alloys. The isotopic measurements were carried out both for the peeling-off part and the remaining non-peeling-off part.

2.3. Analyses

After the electrolysis was finished, the lithium-inserted gallium cathode was taken out of the cell in a dry argon atmosphere, washed thoroughly with dehydrated hexane and was allowed to stand for a day to remove adhering hexane by evaporation. Lithium extraction and isolation from the lithium-inserted gallium electrode and the sample preparation for the mass spectrometric analysis for the ^{7}Li/^{6}Li isotopic ratio were carried out as follows. The cathode was first dissolved with 12 M HCl solution. The HCl concentration of this lithium- and gallium-bearing HCl solution was adjusted to 6 M. Lithium in this HCl solution was separated from gallium by solvent extraction using tributyl phosphate as the organic phase with the 1:1 volume ratio of the aqueous and organic phases. In the solvent extraction, gallium was extracted into the organic phase, while lithium remained in the aqueous phase. The amount of lithium inserted in the gallium cathode was determined by flame photometry. The chemical form of