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Measurement of Self-Diffusion Coefficients in Li Ionic Conductors by Using the Short-Lived Radiotracer of ^{8}Li

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For the effective use of short-lived radioactive beams, soon to be available at the Tokai Radioactive Ion Accelerator Complex, the authors have developed a radiotracer method for diffusion studies in solids. The experimental test was performed by the measurement of the diffusion coefficients of Li in a sample of the compound βLiAl using an α-emitting radiotracer of ^{8}Li ($T_{1/2}$ = 0.84 s). It was found that the time-dependent yields of the α particles from the diffusing ^{8}Li that was initially implanted in the sample could be used as a measure of the diffusivity of the tracer in a nondestructive way. The method was applied to measure the self-diffusion coefficients of Li in βLiGa, and for investigating how the Li diffusion in the Li ionic conductors is affected by the concentration of atomic defects (i.e., the existence of the atomic vacancies of Li and the defects in Ga sites that are replaced by Li).

1. Introduction

At the Tandem accelerator facility of Tokai Institute of Japan Atomic Energy Research Institute, a radioactive ion beam facility, the Tokai Radioactive Ion Accelerator Complex[1] will be operational this year. In the facility, short-lived radioactive ions, produced by proton-induced or heavy ion-induced nuclear reactions, can be accelerated up to the energy necessary for experiments. The energy is variable in the range from 0.1 to 1.1 MeV/atomic mass unit (amu), which is especially efficient for studies on the structural and dynamic properties of the bulk of materials using radioactive ions as tracers. It allows us to implant the radioactive ions into specimens at a proper depth, avoiding the problem caused by the surface (e.g., diffusion barrier-like oxide layers).

In an effort to effectively use the short-lived radioactive ion beams for materials science, a radiotracer method was developed for diffusion studies in solids. In previous reports,[2] the feasibility of the radiotracer method was simulated for diffusion studies using short-lived radioactive ion beams as tracers. Here, the solid material of interest is set at a given temperature and is repeatedly irradiated (implanted) by the energetic tracer beam for a duration of time that is on the order of the half-life of the tracer. Especially when using the α-emitting radiotracer of ^{8}Li (half-life 0.84s), the simulation has shown that the tracer diffusion coefficients in the solid can be measured in a nondestructive and online way, which is completely different from the conventional radiotracer method when used in conjunction with a serial sectioning technique.[3] The time-dependent yields of α particles from the diffusing ^{8}Li have been examined as a direct measure of the diffusion of ^{8}Li in the solid material of interest, reflecting the temporal evolution of the concentration-depth profile of the ^{8}Li primarily implanted in the material.

For the experimental confirmation of this method, an experiment was performed to measure the diffusion coefficients of Li in a sample of βLiAl, through the use of the α-emitting radiotracer ^{8}Li. Using the recoil mass separator (RMS) of JAERI,[4] the ^{8}Li beam was produced for the experiment.

The method has been further applied to measure the self-diffusion coefficients of Li in βLiGa to study how the Li diffusion in the Li ionic conductors is influenced by the concentration of the atomic vacancies of Li as well as the coexistence of different types of defects.

In the following sections, the authors introduce their experimental method: a nondestructive online radiotracer method for diffusion studies in solids using the α-emitting radiotracer of ^{8}Li. This is followed by the preliminary results on the measurement of the self-diffusion coefficients of Li in βLiGa.

2. Experimental Method

After β decay, ^{8}Li emits α particles having a broad energy distribution with an average of 1.6 MeV and 600 keV in a full-width at half maximum (FWHM).[5] In this case, the amount of incidental energy loss from the α particles on their passage to the surface of the solid of interest depends

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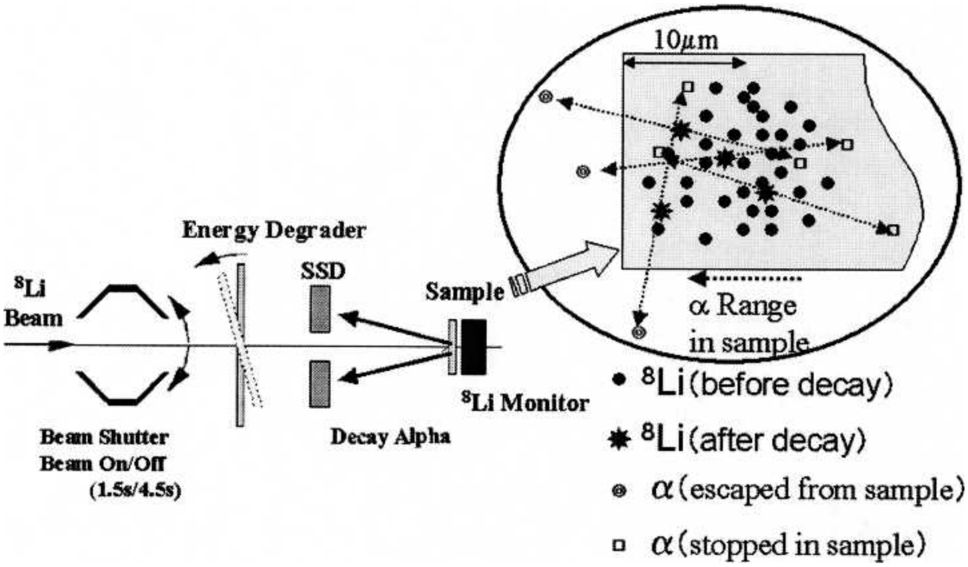

Fig. 1 Schematic of the experimental setup for the measurement of ^{8}Li diffusion coefficients in LiAl. The principle of the measurement is also schematically presented. The yield of α particles measured at a particular time is a measure of the diffused distribution of ^{8}Li primarily implanted in the sample with a depth of about 10 μm.

on the position of the decaying emitter; the measured energies of the α particles emerging from the solid are closely related to the decaying positions of the tracer. The time evolution of the energy spectra is therefore supposed to be a measure of the diffusivity of the tracer in the solid. The energy spectra broaden with increasing diffusion time; the tracer diffusion coefficients could be obtained simply by the time-dependent widths of the measured energy spectra if the inherent energy of the emitted charged particles is well defined. In the present case, however, the inherent energy distribution of the α particles is continuous and broad. Although the correspondence between the emitted position and measured energy of the charged particles is not so simple, as implied in the foregoing, the tracer diffusion coefficient could be obtained with the help of the previously published simulation.[2]

2.1 Experiments

The experimental setup for the diffusion measurement is shown in Fig. 1 and was installed nearly at the focal position of the JAERI-RMS. The radioisotope of ^{8}Li was produced by bombarding ^{7}Li of 24 MeV on a ^{9}Be target of 42 μm thickness. Separated by the JAERI-RMS, an ^{8}Li beam of 14.6 MeV with ~0.6 MeV in FWHM was obtained with an intensity of 2500 particles/s by 30 electric nanoamperes of ^{7}Li. The energy of ^{8}Li for implantation was further reduced to about 4 MeV by the energy degrader installed upstream, corresponding to the average implantation depth of about 10 μm from the front surface of the sample of βLiAl. One time sequence for the measurement consisted of a duration of 1.5 s for implantation (beam-on) and of 4.5 s for subsequent diffusion (beam-off). The beam-on and beam-off operation was carried out by the beam shutter, as shown in Fig. 1. The sample was set at 20 °C (i.e., room temperature) before starting the measurement. It should be noted that the diffusion time mentioned above is different from that of the conventional method because the tracer in the present method diffuses all during the measurement. This is the reason why we call the present method an *online measurement of diffusion*. As schematically shown in Fig. 1, the implanted ^{8}Li decays into two α particles, the average range of which in LiAl is 8 μm. Then, a charged particle detector, located close to the sample surface, could selectively detect α particles from ^{8}Li diffusing toward the sample surface, because the implantation depth is deeper than the range of α particles in the present case. Therefore, the time-dependent yields of α particles with measurable energies are supposed to be sensitive to the Li diffusion in the sample. The α particles coming out of the sample were measured as a function of time by an annular solid-state detector. The sequence was repeated to obtain good statistics, in which time 0 was always at the beginning of the irradiation. We performed the measurement in the same way at temperatures of 150 and 300 °C.

2.2 Data Analysis for Diffusion Coefficients

The yield of α particles with energies of >400 keV showed different time dependence values according to the temperature of the sample. The observation implies that the time dependence of α yields is a good measure of the diffusivity of ^{8}Li in the sample, because the diffusivity depends on the temperature of the sample. By excluding the trivial time dependence of the yields associated with the radioactive lifetime of ^{8}Li during the measurements, the authors obtained the time spectra only depending on the temporal evolution of the profiles of diffusing ^{8}Li at a temperature of the sample. In Fig. 2, the time spectra that were measured at different temperatures (i.e., 20, 150, and 300 °C) are represented by ratios (i.e., the yields of α particles divided by those of ^{8}Li existing in the sample at the time of interest). If ^{8}Li did not diffuse at all, the spectra should be constant over time. However, the experimental values of the

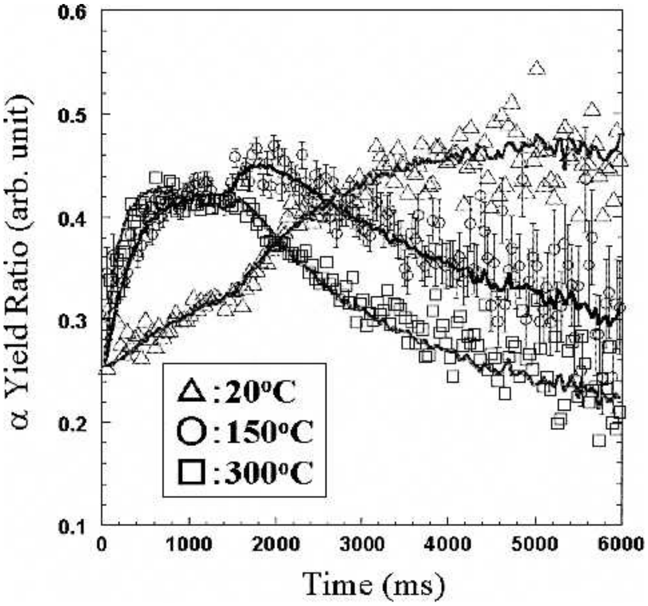

Fig. 2 Normalized time spectra of α yields from βLiAl obtained at the indicated temperatures. The results from the simulation are also shown as solid lines. In the simulation, best reproducing the data as a result of χ^2 tests, the diffusion coefficients of 7.5×10^{-8}, 5.6×10^{-7}, and 1.3 × 10−6 cm_2/s were assumed at 20, 150, and 300 °C, respectively.

ratios gradually increase with time, demonstrating well that with increasing time, and depending on the diffusivity the α-emitting ^{8}Li, more α particles are coming out of the sample; otherwise the α particles are stopped in the sample and thus are not detected.

By comparing an experimental normalized time spectrum (time-dependent ratio) obtained at a certain temperature with those simulated with different diffusion coefficients, a diffusion coefficient at the temperature could be finally obtained. The time spectra that were simulated with the diffusion coefficients best reproducing the experimental data at the respective temperatures as a result of the comparisons are presented in Fig. 2.

Here, the authors briefly describe the simulation and the process of the comparisons between the simulated and experimental spectra to extract diffusion coefficients. In the simulation, as described in detail in Ref 2, first defined was the incident energy and energy spread of the ^{8}Li beam from the energy spectrum measured at the instant of implantation. Using the incident condition of the beam, a simulation of the concentration-depth profile of ^{8}Li implanted in the sample and the time evolution of the profile when a certain diffusion coefficient of Li in the sample was assumed. And then, as a measure of Li diffusion in the sample, the energy spectra of α particles emitted from the time-dependent profiles of ^{8}Li were simulated by referring to the energy loss and straggling on their passage from the emitted position to the sample surface. Finally, the time-dependent α particle yields, which depend on the diffusion coefficients assumed in the simulation, were obtained. They were compared with the experimental time spectra shown in Fig. 2 after they were normalized in the same manner as the experimental data. The parameters (i.e., the mean and FWHM) describing the concentration-depth profile and the energy loss and straggling of α particles were estimated by using the SRIM-2003 code,[5] which is widely used in this kind of application with high reliability.

In the comparisons, the authors performed χ^2 tests; the comparison of the experimental time spectrum versus the simulated spectrum was taken as a measure of maximum likelihood. In the case of maximum likelihood, the reduced χ^2 value, the value of χ^2 simply divided by the number of data points in the present case, should be approximately equal to 1. The diffusion coefficient assumed in the simulation that shows the maximum likelihood of the time dependence measured at a certain temperature was adopted. The absolute scales of the ordinate in Fig. 2 are arbitrary, but are relatively correct in different measurements. Once the parameters in the simulations were adjusted to reproduce the data at a given temperature (e.g., 150 °C in the present case), what remains for further comparisons with the data measured at different temperatures are, accordingly, only the variations of the diffusion coefficients. The parameters for the first fine adjustment include the absolute scale, the implantation depth, the width of the primary concentration profile of the tracer, and the energy threshold of the α particles. Among these parameters, the implantation depth was found to be the most sensitive, and the authors could not reproduce the experimental time dependence using the depth estimated by the SRIM-2003 code.[5] The resultant depth is shorter than the estimated value by about 5% in the target matrix of Al (energy degrader) and LiAl at the incident energy of 14.6 MeV and by about 17% in LiAl at 4 MeV. This is another interesting aspect of the measurement; the present method could be applied as a range meter of Li isotopes in the compound in which the Li diffusion coefficients are well known. On the other hand, it is a disadvantage of the present method because an additional, not well-defined parameter should be taken into account in the simulation to extract unknown diffusion coefficients. Consequently, the accuracy of the diffusion coefficients finally obtained in the manner mentioned above is, to a large extent, reduced. Although a more deliberate analysis for estimating the accuracy is necessary, one can preliminarily conclude that the diffusion coefficients could be extracted with an accuracy of 25%, especially at room temperature where a rather large discrepancy was observed in the comparison, as shown in Fig. 2. The accuracy could be improved by the more detailed measurements (i.e., varying the temperatures in smaller steps than those in the present experiment).

As the reference spectrum for normalization, an experimental time spectrum of the α radioactivity of ^{8}Li implanted in pure Al was used. It allows us to avoid the systematic errors caused by the beam-on/beam-off operations, because no measurable diffusion effects were observed in this case.

3. Li Diffusion in βLiGa

The β phase of intermetallic Li compounds such as βLiAl, LiGa, and LiIn has been considered as a possible electrode material in Li ionic batteries due to the high diffusion coefficients at room temperature of Li ions.[6] They all crystallize with the NaTl structure,[7] which consists of two interpenetrating sublattices, each forming a diamond lattice. Homogeneity ranges near the equatorial atomic ratio have been reported (48 ~ 56 at.% Li for LiAl, 44 ~ 54% at.% Li for LiGa, and 44 ~ 54 at.% Li for LiIn). To understand the motion of Li in the β phase, as an ionic conductor, the defect structure in the Li compounds was intensively studied via the measurement of electrical resistivity and density with help of the standard x-ray diffraction analysis.[8,9] This defect structure is closely related to the fast ionic motion. There exist three kinds of defects: vacancies on Li sites (V_{Li}); defects on antisites that replace atoms by Li (Li$_A$ [A = Al, Ga, and In]); and complex defects (V_{Li}-Li$_A$ complex). By forming the complex defects, the ionic motion of Li is suppressed or assisted depending on the kinds of antisite atoms; Li diffusion rather slows down in βLiAl while it becomes rather faster in βLiIn, although Li diffusivity almost linearly depends on the constitutional vacancy concentration on the Li sublattice (V_{Li}).[10] The high diffusion coefficient in the Li compounds is associated with the constitutional vacancy concentration on the Li sublattice, which is relatively large compared with that of the usual metal alloy. The thermodynamic behavior of the Li vacancy has also been inferred from the anomalous electrical resistivity (i.e., the "100 K" anomaly) observed at about 95 K near the critical composition corresponding to the Li-deficient region of βLiAl[11] and is considered to be an order-disorder transition of vacancies on the Li sublattices.[12]

The macroscopic ionic motion of Li has so far been inferred from the analysis of the electrical response to the applied voltage (i.e., the electrochemical method).[13] The values of diffusion coefficients, which were essentially obtained in such indirect ways, are often scattered over several orders of magnitude, strongly depending on the method of data analysis for the finally extraction of the diffusion coefficients.

In such a general situation, the authors applied their method for measuring diffusion coefficients of Li in βLiGa, in which the diffusion coefficients have not been well measured, although Li diffusion is known to be fastest among the Li intermetallic compounds. The high diffusivity of Li in βLiGa is associated with an especially large, constitutional vacancy concentration on the Li sublattice that is almost three times larger than that in βLiAl.

It would be very interesting to observe, directly in terms of diffusion coefficient, the order-disorder transition of the vacancies on Li sites as well as the effect on the Li diffusion associated with the formation of the complex defects.

Diffusion measurement was performed for βLiGa by using the experimental setup shown in Fig. 1. The preliminary experimental results will be presented in the next section.

The βLiGa compounds with Li atomic compositions of 44%, 51%, and 54% were used in this study and were prepared by direct reaction of the desired amounts of Li and Ga, as reported in Ref 9.

3.1 Order-Disorder of Li Vacancies

To observe the order-disorder transition of vacancies on Li sites in terms of the self-diffusion of Li, a detailed measurement was performed below room temperature for the βLiGa at 44 at.% Li, the most Li-deficient composition of the β phase of LiGa. Indeed, a sudden change in the Li self-diffusion coefficients is observed at about 240 K, as shown in Fig. 3, at which temperature the anomalous electrical resistivity has been observed.

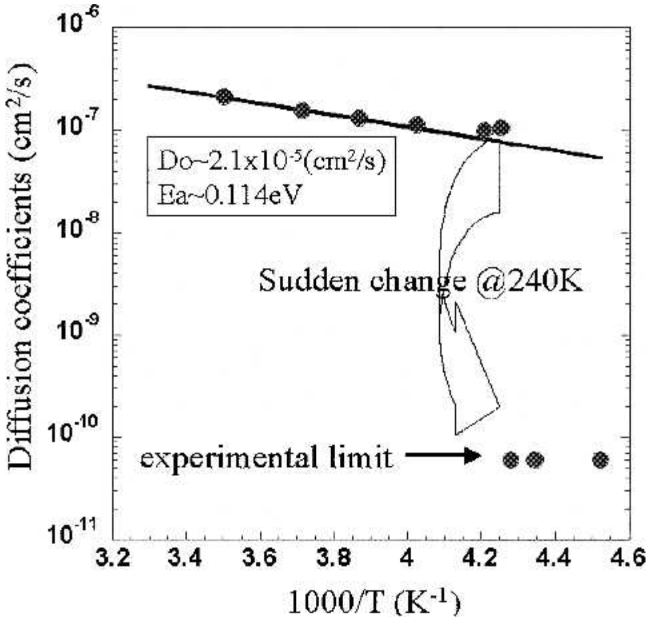

Fig. 3 Arrhenius plot of the diffusion coefficients measured in βLiGa (44 at.% Li). The solid line represents the data fitted with a single exponential of $Do \times \exp(-Ea/T)$, where Do is the prefactor (i.e., the frequency factor) and Ea is the activation energy for diffusion.

Figure 3 shows the temperature dependence of Li diffusion coefficients in βLiGa (44 at.% Li) obtained by using a short-lived radiotracer of ^{8}Li. At about 240 K, a sudden change in the value of the diffusion coefficients is observed. In the higher-temperature region, the diffusion coefficients follow Arrhenius behavior. In the lower-temperature regions, the diffusion coefficients are observed to be constant at the lower limit of diffusion coefficients accessible by our present method; for diffusion coefficients less than about 10^{-10} cm^2/s, any significant effect in the α particle yields due to the diffusing ^{8}Li could not be observed because of the short lifetime of the radiotracer.

Around the transition temperature, the time structure of the normalized α particle yields could not be explained in terms of one component of diffusion (i.e., one diffusion coefficient), implying that the diffusion coefficients would not be singly determined in the transition region. The temperature window, in which the transition appears to occur, is at about 10 K.

By the neutron diffraction measurements for βLiAl,[12] a sudden change in the electrical resistance at about 100 K has been understood by an ordering of the vacancies on the Li sublattice. The structure below 100 K is body-centered tetragonal; the unit cell contains 10 Li and 20 Al positions, with the vacancies located at 2a positions. An ordering of

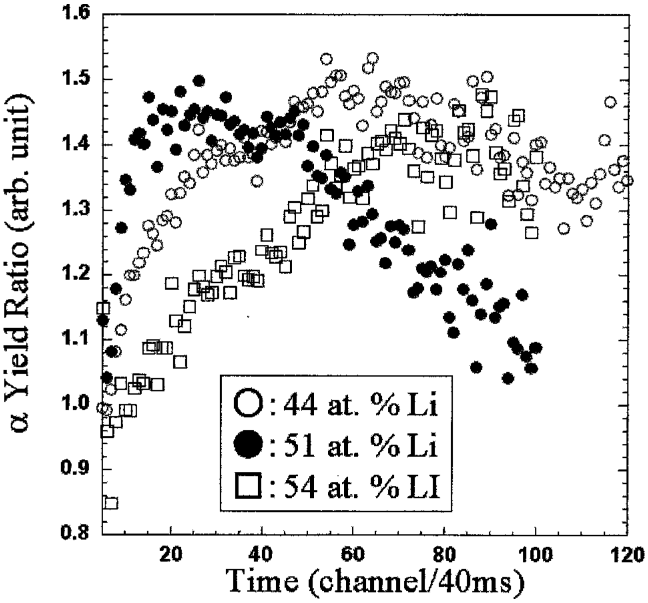

Fig. 4 Normalized time spectra of α yields from βLiGa obtained with different Li compositions as indicated in this figure. The temperature was set at room temperature. The time spectrum, more rapidly rising and falling with increasing diffusion time, corresponds to a faster diffusion of Li.

the vacancies would produce a sharp drop in the Li diffusion coefficients at the ordering temperature. The observed amount of change, which is more than two orders of magnitude in the value of diffusion coefficients, is quite impressive compared with those observed in the measurement of electrical resistivities. Therefore, with higher sensitivity to the transition, the present method could be applied for better investigating the characteristics of the transition that are supposed to be correlated with the Li composition and the number of Li vacancies.

3.2 Li Composition Dependence of Li Diffusion

The concentration of the vacancies on the Li sites strongly depends on the Li compositions[9]; this vacancy concentration is about 12% for the most Li-deficient βLiGa and about 3% for the most Li-excessive βLiGa. V_{Li} is the dominant defect for Li-deficient compositions, Li_{Ga} is the dominant defect for the Li-excessive compositions, and the mixing of the two defects extends throughout the entire phase region. The coexistence in V_{Li} of Li_{Ga} is expected to form the V_{Li}-Li_{Ga} complex defects, as reported in Ref 8 and 9 for the defect structure of βLiAl. Especially, almost the same amounts of V_{Li} and Li_{Ga} exist for the composition of 51 at.% Li.

In Fig. 4, the time-dependent normalized α particle yields are compared for different Li compositions (i.e., 44, 51, and 54 at.% Li). Referring to the time dependence of the α particle yields, βLiGa with the Li composition of 51 at.% shows the fastest diffusion of Li among three. This observation is quite different from those for βLiAl and LiIn, in which, as the Li compositions decrease, the Li diffusion becomes faster with a minor modification due to the coexistence of V_{Li} and Li_{Ga}. In the case of βLiGa, more constitutional vacancies on the Li sites exist for a fixed Li composition compared with those of βLiAl and LiIn, and accordingly more defects of Li_{Ga} are expected to exist. The motion of the vacancies on Li sites, supposedly the carriers of Li atoms, seems to be strongly promoted by the presence of antisite defects Li_{Ga}. In other words, the interaction between V_{Li} and Li_{Ga} would be unexpectedly large compared with analogous defects in βLiAl and LiIn. More detailed experiments are going to be performed along these lines.

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