MLF Experimental Report	提出日 Date of Report January 06, 2010
課題番号 Project No. 2009A0031 実験課題名 Title of experiment Lithium diffusion in lithium-transition-metal-oxides 実験責任者名 Name of principal investigator Jun Sugiyama 所属 Affiliation Toyota Central Research and Development Laboratories, Inc.	装置責任者 Name of responsible person Yasuhiro Miyake 装置名 Name of Instrument/(BL No.) D1 実施日 Date of Experiment June 10, 2009 - June 13, 2009

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Lithium nickel dioxides, $Li_{1-x}Ni_{1+x}O_2$ with x~0.07.
A powder sample was pressed in a disc with 30 mm diameter and 2 mm thickness, and then the disc was packed in an Au-sealed cell.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

In order to detect the diffusion coefficient of Li+ ions (D_{Li}) in $LiNiO_2$, which are heavily investigated as a cathode material for the next-generation Li-ion batteries, we have measured wTF-, ZF-, and LF-μSR spectra for $LiNiO_2$ in the temperature range between 60 and 450 K. Here, it should be noted that, in the rhombohedral $LiNiO_2$ lattice with space group *R*3-m, the NiO_2 plane and the Li layers form alternating stacks along the c_H-axis in the hexagonal setting (see Fig. 1). In the NiO_2 planes, Ni ions form a two-dimensional triangular lattice (2DTL) by a network of edge-sharing NiO_6 octahedra. In contrast to $LiCoO_2$, a stoichiometric $LiNiO_2$ has never been prepared so far. That is, the excess Ni is usually present in the Li layer of the $LiNiO_2$ samples due to the similarity in ionic radii between Li^+ and Ni^{3+}. The ionic distribution of the Ni-excess $LiNiO_2$ is thus given by $(Li^+_{1-x}Ni^{2+}_x)_{3b}[Ni^{2+}_xNi^{3+}_{1-x}]_{3a}O_2$, where 3*b* and 3*a* are the Li and Ni site in the regular $LiNiO_2$ lattice. Besides of an interesting change in low-*T* magnetism of $Li_{1-x}Ni_{1+x}O_2$ with *x*, the $(Ni^{2+})_{3b}$ ions are naturally expected to affect D_{Li} at high *T*, because of planer hindrance of $(Ni^{2+})_{3b}$ in the Li layer, in which Li^+ ions move relatively easily. Nevertheless, there is, to authors'.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

knowledge, less systematic work on the relationship between D_{Li} and x, mainly due to lack of a proper tool for detecting D_{Li}. The μSR experiment on $Li_{1-x}Ni_{1+x}O_2$ with x~0.03, ~0.07, and ~0.15, therefore, provides crucial information on the effect on D_{Li}, resulting in clear insight how to improve cathode materials.

Following upon the experiment on the x~0.03 and ~0.15 samples in February of 2009, we attempted to measure μSR spectra for the x~0.07 sample, which was prepared by heating the x~0.03 sample at 850°C. The ZF- and LF-spectra were well fitted by a dynamic Kubo-Toyabe function, as in the case for the previous two samples. By using a global fit technique for ZF-, LF-, and wTF-spectra, the field distribution width (Δ) and field fluctuation rate (ν) for the x~0.07 sample were estimated at each temperature (red circles in Fig. 2). Surprisingly, ν of the x~0.07 sample is found to be almost T-independent up to the highest T measured (450°C), although Δ decreases with T as observed for the other two samples.

Based on the previous results, ν for the x~0.03 and ~0.15 samples increased with T, as expected. Also, the increase in ν with T for the x~0.15 sample was suppressed compared with that for the x~0.03 sample, being consistent with the planer hindrance of the Ni ions in the Li layer. Therefore, it is very difficult to explain the ν(T) curve for the x~0.07 sample, although ν would exhibit a complex dependence on x. In order to confirm the result on the x~0.07 sample and to add T points for the x~0.15 sample, we plan to continue the experiment in the winter of 2009/2010.

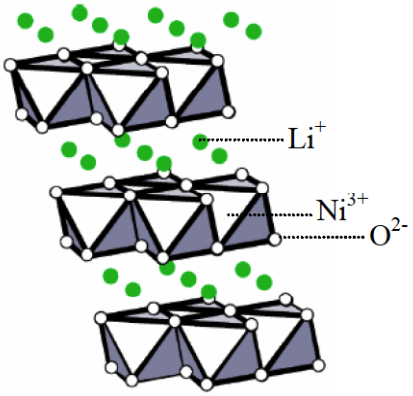

Fig.1 The crystal structure of $LiNiO_2$.

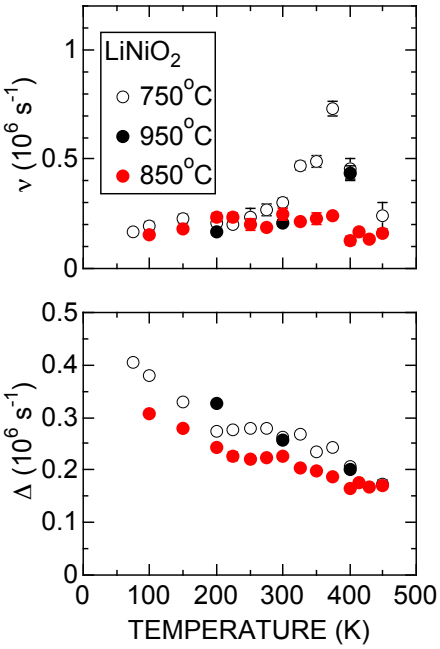

Fig. 2 T dependences of (top) field fluctuation rate ν and (bottom) field distribution width Δ for $Li_{1-x}Ni_{1+x}O_2$ with x~0.03 (open circles), ~0.07 (red), and ~0.15 (black). The data were obtained by global-fitting the ZF-, LF-, and wTF-spectra.