**Li-ion diffusion in Li-ion battery material LiFe$_{1-x}$Mn$_x$PO$_4$**

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For the development of on-board batteries, the Li-ion battery is required to operate at high voltages. For realizing a practical Li-ion battery, a solid solution of the olivine-type lithium iron/manganese phosphate (LiFePO$_4$ and LiMnPO$_4$) is used as the positive electrode material. Olivine lithium phosphate is superior in terms of stability and is a low cost material. The tetrahedron PO$_4$ is so stable that oxygen desorption hardly occurs. Compared to other positive electrode materials such as LiCoO$_2$, olivine lithium phosphate is produced at a low cost because it contains no transition metals. High charge/discharge voltage can be steadily obtained for the Li(Fe,Mn)PO$_4$ solid solution. It is noted that the LiFe$_{1-x}$Mn$_x$PO$_4$ ($x$=0.7) solid solution is used for the realization of a practical Li-ion battery.

LiFePO$_4$ by $\mu^+$SR$^1)$. However, we could not obtain information about Li diffusion for LiMnPO$_4$, because $\mu^+$SR spectra were strongly affected by magnetic moment of Mn$^{2+}$. Although the diffusive nature of Lithium is represented in the dynamic Kubo-Toyabe (KT) type relaxed signal in zero field (ZF) $\mu^+$SR measurements, the small changes in KT signal are hidden by fast relaxed signal caused by the magnetic moment of Mn$^{2+}$. In order to avoid the magnetic effect due to Mn$^{2+}$, we measured $\mu^+$SR spectra on LiFe$_{1-x}$Mn$_x$PO$_4$ with smaller $x$ to presume the Li diffusive nature in LiFe$_{1-x}$Mn$_x$PO$_4$ with larger $x$ (Fig. 1).

In order to investigate Li-ion diffusion in the solid solution similar to the one used in the practical battery, we measured $\mu^+$SR spectra on LiFe$_{0.2}$Mn$_{0.8}$PO$_4$. In $x$=0.8 samples, the ZF-$\mu^+$SR spectrum is fitted by the sum of the exponentially relaxed static KT function and fast relaxation, assuming the volume fraction determined for smaller $x$ as the initial value. Then, the ZF-$\mu^+$SR spectrum exhibits dynamic KT function at temperatures above 150 K. By fitting the ZF- and LF-spectra with a dynamic KT function, the field fluctuation rate ($\nu$), relaxation rate ($\lambda$) and the field distribution width ($\Delta$) were obtained. For $x$=0.8, $\nu$ rapidly starts to increase and $\Delta$ starts to decrease at 150 K (Fig. 2). This indicates that Li-ion diffusion occurs above 150 K. The diffusion coefficient is estimated as $D_{Li} = 2.1 \times 10^{-10}$(cm$^2$/s) at 300 K.

By utilizing ARGUS spectrometer to obtain a large asymmetry for the KT signal, we obtained additional data to the systematic results taken with EMU spectrometer for the solid solution, LiFe$_{1-x}$Mn$_x$PO$_4$ with $x=0.2 - 1$. There appers to be a peak in $D_{Li}$ between $x$=0.6 and $x$=1 (Fig. 1). However, we cannot conclude that $D_{Li}$ has a small peak around $x$=0.8 since we have measured only for $x$=0.6 and 0.9. We would like to study in detail the region between $x$=0.6 - 0.9, since the composition is very close to that used in a practical Li-ion battery.

We also measured $\mu^+$SR spectrum on $x$=0 sample, however, the obtained data was unsatisfactory. It is reported in Ref. 1 that $D_{Li} = 3.6 \times 10^{-10}$(cm$^2$/s) at 300 K. Since $D_{Li}$ changes drastically between $x=0$ and 0.2, we need to try to confirm such large changes.

The activation energy $E_a$ was estimated from the relation $E_a=k_B\ln(\nu)$ to be 53.0 meV for $x=0.8$. There may be a peak in $E_a$ between $x=0.6$ and 1 (not shown).

Reference