

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

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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 $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ solid solution. It is noted that the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x\sim 0.7$) solid solution is used for the realization of a practical Li-ion battery.

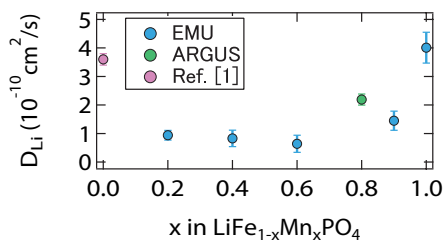


Fig. 1. x dependence of the D_{Li} at 300 K. The data for $x = 0$ is reported in Ref. 1 and the data for $x = 0.2, 0.4, 0.6, 0.9$ and 1 have been obtained with EMU spectrometer in ISIS.

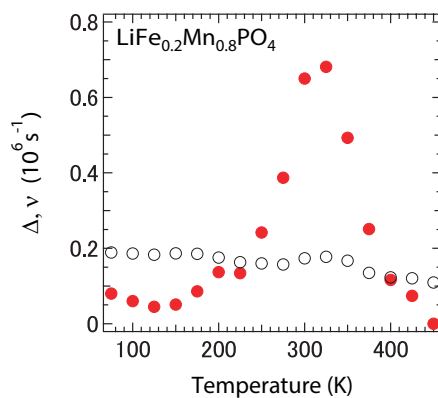


Fig. 2. Temperature dependences of (a) Δ (open circle) and (b) ν (closed circle) obtained for $\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$.

We investigated Li diffusion in LiFePO_4 and

LiMnPO_4 by $\mu^+\text{SR}$ ¹⁾. However, we could not obtain information about Li diffusion for LiMnPO_4 , because $\mu^+\text{SR}$ 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) $\mu^+\text{SR}$ 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 $\mu^+\text{SR}$ spectra on $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ with smaller x to presume the Li diffusive nature in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ 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 $\mu^+\text{SR}$ spectra on $\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$. In $x=0.8$ samples, the ZF- $\mu^+\text{SR}$ 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- $\mu^+\text{SR}$ 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 (ν), relaxation rate (λ) and the field distribution width (Δ) were obtained. For $x=0.8$, ν rapidly starts to increase and Δ starts to decrease at 150 K (Fig. 2). This indicates that Li-ion diffusion occurs above 150 K. The diffusion coefficient is estimated as $D_{\text{Li}} = 2.1 \times 10^{-10} (\text{cm}^2/\text{s})$ 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, $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ with $x = 0.2 - 1$. There appears 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 $\mu^+\text{SR}$ spectrum on $x=0$ sample, however, the obtained data was unsatisfactory. It is reported in Ref. 1 that $D_{\text{Li}} = 3.6 \times 10^{-10} (\text{cm}^2/\text{s})$ 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 $E_a = k_B T \ln(\nu)$ 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

- 1) J. Sugiyama et al., Phys. Rev. B **85**, 054111 (2012).

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