Li-ion diffusion in $LiFeSi_xP_{1-x}O_4/C$ with $x = 0$ and 0.03

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The primary issue in the use of $LiFePO_4$ in battery applications is its low intrinsic electronic conductivity and lithium-ion diffusion coefficient. Furthermore, there is an urgent need to improve the cycle life and long-term cyclability of $LiFePO_4$.[1)] Several strategies have been considered to enhance the electronic/ionic conductivity and cycle life of $LiFePO_4$, such as carbon coating, reduction of particle size, and element doping.[2)]

Powder samples of $LiFeSi_xP_{1-x}O_4/C$ with $x = 0$ and 0.03 were prepared by a solid-state method. Single-phase samples of $LiFePO_4$ have not been obtained so far. Our study strongly supports that Si doping significantly improves the electrochemical performance of $LiFePO_4$ as reported in Ref. 3). A sample with $x = 0.03$ yielded the highest specific capacity. Further study on Li-ion diffusion is significant for increasing the battery performance. Muon spin relaxation (μSR) is a powerful tool to study Li-ion diffusion.

In order to study the Li-ion diffusion in $LiFeSi_xP_{1-x}O_4/C$ further, we measured zero-field and longitudinal-field μSR (ZF- and LF-μSR, respectively) using the ARGUS spectrometer at the RIKEN-RAL Muon Facility. The ZF-μSR was measured in the temperature range of 5–30 K, and the LF-μSR was measured at 300 K under low magnetic fields of 5 G and 10 G.

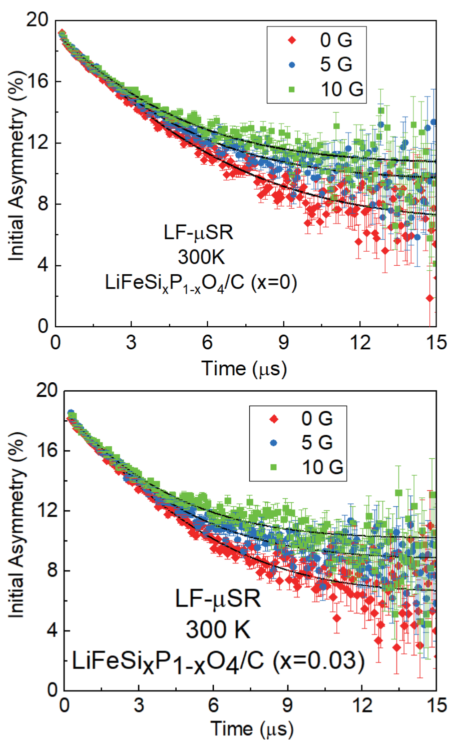

Fig. 1. LF-μSR spectra on of $LiFeSi_xP_{1-x}O_4/C$ with (a) $x = 0$ and (b) $x = 0.03$.

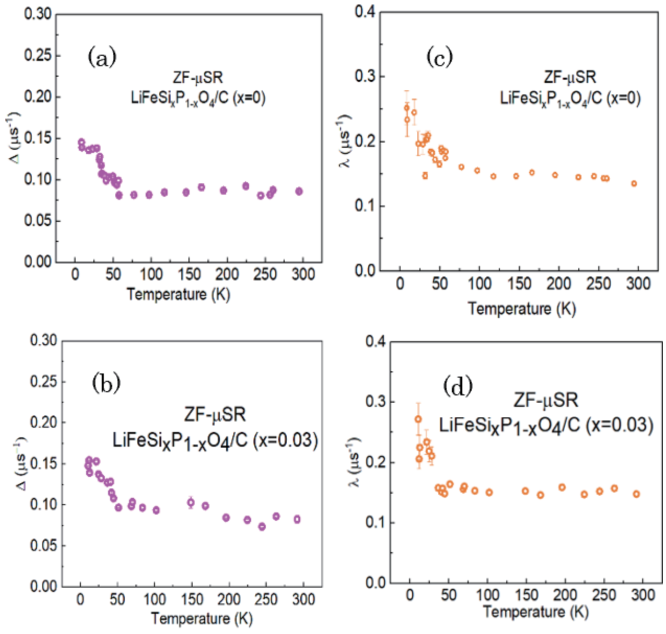

Fig. 2. Temperature dependences of Δ with (a) $x = 0$ and (b) $x = 0.03$ and of λ with (c) $x = 0$ and (d) $x = 0.03$ for $LiFeSi_xP_{1-x}O_4/C$.

Figure 1 shows the LF-μSR spectra of $LiFeSi_xP_{1-x}O_4/C$ with (a) $x = 0$ and (b) 0.03. The dynamic behavior at 300 K was clearly observed for $LiFeSi_xP_{1-x}O_4/C$ with $x = 0$ and 0.03 because there is only a small "decoupling" effect due to applied LF. The spectra were fitted by an exponentially relaxing dynamic Kubo-Toyabe function.

Based on Fig. 2, the field distribution width (Δ) and field fluctuation (λ) were found to be independent of temperature down to 50 K, whereas Δ and λ increased with temperature decreasing below 50 K for samples with $x = 0$ and $x = 0.03$. There is no abrupt change in Δ or λ in either sample. Following the results in Ref. 4), we obtained the diffusion coefficient as $D_{\rm Li} = (1.598 \pm 0.0033) \times 10^{-10}$ cm^2/s, for $x = 0$ and $D_{\rm Li} = (1.751 \pm 0.0037) \times 10^{-10}$cm^2/s for $x = 0.03$. The present result demonstrates the slight increase of Li-ion diffusion by silicon substitution, which can improve the performance of $LiFePO_4$ cathode materials. Additionally, from the ZF-μSR results, the magnetic transition temperature was detected, starting from the temperature 50 K and close to the estimation of the Neel temperature, $T_{\rm N}$, $LiFePO_4$ reported in Ref. 5).

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