Li-ion diffusion in Li_xFePO_4 with $x = 0$, 0.25 and 0.5

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Lithium iron phosphate, $LiFePO_4$, is used as a cathode material in Li-ion batteries. A comparison with the conventional cathode materials such as $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ showed that $LiFePO_4$ has a special advantage over because of its high stability during the lithium extraction/intercalation reaction at medium temperatures (around 400 K).

Based on electrochemical[1,2] and structural analyses,[3] the lithium extraction reaction from $LiFePO_4$ is represented as follows: $LiFePO_4$ - xLi → $(1 - x)LiFePO_4$ + $xFePO_4$. Both $LiFePO_4$ and $FePO_4$ phases coexist in Li_xFePO_4, and single phase samples of Li_xFePO_4 have not been obtained so far. Following upon the μ^+SR work on $LiFePO_4$,[4] we have measured μ^+SR spectra on Li_xFePO_4 ($x = 0$, 0.25, and 0.5) in order to understand the diffusive property shown in Li_xFePO_4 sample consisting of the two phases.

Powder samples of Li_xFePO_4 were prepared from $LiFePO_4$ by reacting it with NO_2BF_2 in acetonitrile. Then, the Li-deficient powder sample was sealed into a titanium cell with a gold o-ring. The window of the cell was made of a Kapton film of 50 μm thickness. The cell was mounted onto the Cu plate of a liquid-He flow-type cryostat in the temperature range between 10 and 400 K.

Figure 1 shows the temperature dependence of zero field (ZF-) and longitudinal field (LF-) μ^+SR spectra for $FePO_4$. Since there is no crucial change with temperature, the implanted muons are static up to 250 K. In fact, the spectra were fitted by a combination of a dynamic Kubo-Toyabe (KT) signal and a time-independent background signal from a powder cell. The field distribution width (Δ) and the field fluctuation (ν) were found to be independent of temperature; $\Delta_{FePO4} = 7.1 \times 10^4$ s^{-1} and $\nu_{FePO4} = 2.6 \times 10^4$ s^{-1}.

On the other hand, dynamic behavior was clearly observed for $Li_{0.25}FePO_4$ and $Li_{0.5}FePO_4$. The μ^+SR spectra were well fitted by a combination of two KT signals and a background signal. The two KT signals came from the muons stopped in the $LiFePO_4$ phase and those in the $FePO_4$ phase. Therefore, we used the same values of Δ_{FePO4} and ν_{FePO4} for the KT signal from the $FePO_4$ phase. Figure 2 shows the temperature dependence of Δ and ν for the three samples. As expected, the result is very consistent with that obtained for $LiFePO_4$. Assuming that the Li-ion jump to interstitial sites,[4] we obtained the diffusion coefficient as: $D_{Li} = 5.8 \times 10^{-11}$ cm^2/s at 200 K for $Li_{0.5}FePO_4$ and $D_{Li} = 1.3 \times 10^{-11}$ cm^2/s for $Li_{0.25}FePO_4$. These values are smaller than D_{Li} for $LiFePO_4$,[4] implying the effect of Li-ion diffusion between the $LiFePO_4$ and $FePO_4$ phases. Such interphase diffusion is believed to be the most interesting process shown in the $LiFePO_4$ cathode. In order to understand the interphase Li-ion diffusion, however, we need to study the relationship between D_{Li} and x in Li_xFePO_4 in more detail.

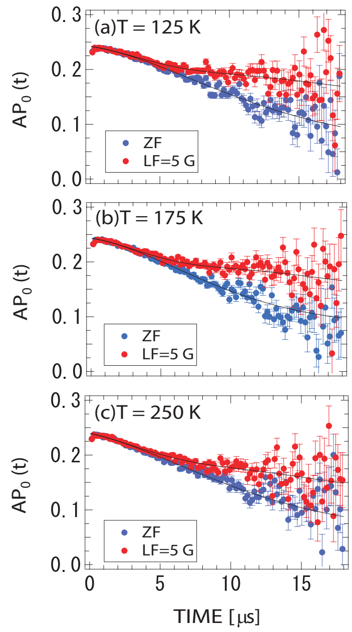

Fig. 1. ZF- and LF-μ^+SR spectra on $FePO_4$ at (a) 125 K, (b) 175 K, and (c) 250 K.

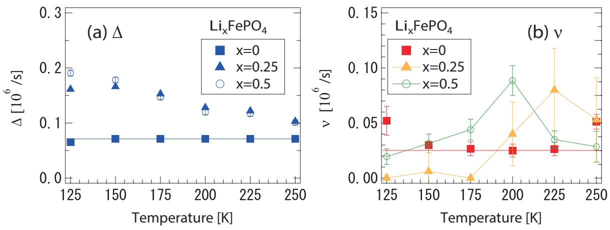

Fig. 2. Temperature dependence of (a) Δ and (b) ν obtained for $FePO_4$, $Li_{0.25}FePO_4$, and $Li_{0.5}FePO_4$.

References
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