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Mechanistic insights of Li⁺ diffusion within doped LiFePO₄ from Muon Spectroscopy

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The Li⁺ ion diffusion characteristics of V- and Nb-doped LiFePO₄ were examined with respect to undoped LiFePO₄ using muon spectroscopy (μ SR) as a local probe. As little difference in diffusion coefficient between the pure and doped samples was observed, offering D_{Li} values in the range $1.8\text{--}2.3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, this implied the improvement in electrochemical performance observed within doped LiFePO₄ was not a result of increased local Li⁺ diffusion. This unexpected observation was made possible with the μ SR technique, which can measure Li⁺ self-diffusion within LiFePO₄, and therefore negated the effect of the LiFePO₄ two-phase delithiation mechanism, which has previously prevented accurate Li⁺ diffusion comparison between the doped and undoped materials. Therefore, the authors suggest that μ SR is an excellent technique for analysing materials on a local scale to elucidate the effects of dopants on solid-state diffusion behaviour.

Spin-polarised muons can be used as a local probe to investigate the solid-state diffusion behaviour of Li-ion battery materials. The diffusive processes within these materials are not always well understood and muons can provide detailed insight into the Li⁺ diffusion mechanisms^{1–3}. The sensitivity of the embedded muon to local magnetism (through the time-evolution of its spin polarisation) has been utilised to investigate many properties of solid state materials, such as hydrogen diffusion, magnetism and radical chemistry^{1–3}. Similarly, Li⁺ diffusion within a sample, perturbs embedded muons and the Li⁺ diffusion coefficient can be extracted from analysis of this perturbation. This technique has successfully determined the Li-ion diffusion coefficients in LiCoO₂⁴, bulk LiFePO₄^{5–7}, nano-LiFePO₄⁸, and the Li_{6.5}Al_{0.25}La_{2.92}Zr₂O₁₂ solid-state electrolyte material⁹. Indeed, μ SR has successfully determined consistent experimental diffusion coefficients of Li⁺ in pure LiFePO₄ in the range 10^{-10} to $10^{-9} \text{ m}^2 \text{ s}^{-1}$, in good agreement with theoretical studies, but to the authors' knowledge has not been extended to V- or Nb-doped LiFePO₄ systems previously^{5–8}.

LiFePO₄ (and doped variants) have been extensively investigated as a cathode material for Li-ion batteries, as it offers a more sustainable alternative to cobalt-based cathodes such as LiCoO₂ and LiNi_xMn_yCo₂O₂¹⁰. Historically, LiFePO₄ initially suffered from poor Li insertion/extraction kinetics¹¹, efforts to nanosize^{12,13}, carbon-coat^{14–16}, and dope the material have often improved the attainable storage capacity, particularly at high charge/discharge rates. In particular, aliovalent doping of LiFePO₄ with transition metal ions such as V³⁺ and Nb⁵⁺ has been a successful strategy for improving the resulting electrochemical performance^{17,18}, although there is a lack of consensus on the precise reasons for this. Many authors have observed distortions of the unit cell^{19–22}, and widening of the 1D diffusion channels in the material, which was suggested as a mechanism for lowering the activation energy for Li-ion diffusion. There is also some argument as to whether the dopants create defects in the material (such as Li vacancies) that boost diffusion²⁰. Furthermore, the dopant may alter the electronic conductivity and consequently improve performance¹⁸. The subtle effects of dopants on atomic structure can be difficult to observe in great detail using standard lab based analytical techniques, and therefore, alternative methods must be sought to fully understand the effects of doping on electrode materials.

Herein, we report our investigations into Li⁺ diffusion within LiFePO₄, Nb- and V-doped LiFePO₄. The two doped LiFePO₄ samples both displayed enhanced cycling performance at high discharge rates in comparison with

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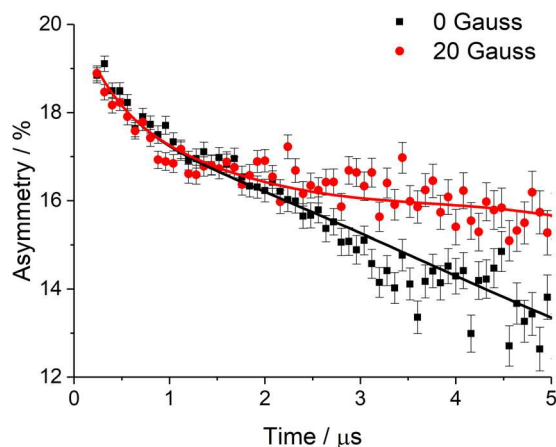


Figure 1. Representative muon decay asymmetry for sample δ LFP, showing the raw data with the fit overlaid, as a function of time at various magnetic fields.

the undoped LiFePO_4 sample^{21,23}, and the μ SR results allowed the unambiguous comparison of Li-ion mobility on a local level within these samples. This increased insight into Li^+ diffusion processes present the future possibility of optimising doped compositions to give improved Li-ion battery performance.

Methods

The synthesis of pure LiFePO_4 , Nb- and V-doped LiFePO_4 materials have been described in detail in previous publications^{21,23}. Briefly, these carbon-coated lithium iron phosphate samples (where the C is amorphous) were synthesized using a pilot-scale continuous hydrothermal flow synthesis (CHFS) reactor, described in detail in the Supporting Information and elsewhere²⁴. These samples were heat-treated at 700°C for 3 h (5°C min^{-1} ramp rate) to graphitize the carbon coatings. Undoped LiFePO_4 was selected for muon analysis as a control as well as the optimal performing dopant compositions of $\text{LiFe}_{0.99}\text{Nb}_{0.01}\text{PO}_4$ and $\text{LiFe}_{0.95}\text{V}_{0.05}\text{PO}_4$, which were named δ LFP, δ LFNP(1.0) and δ LFVP(5), respectively (the δ term denotes these samples were heat-treated).

The μ SR experiments were conducted at the ISIS pulsed muon and neutron source on the EMU instrument²⁵. The data were analysed using the Windows Muon Data Analysis (WiMDA) program²⁶. These samples were prepared for analysis by transferring *ca.* 1 g into Ti cavities with a Ti foil window. Ti was chosen as a sample holder material because it has negligible internal magnetic fields and therefore gave a simple background feature which could be easily subtracted in the analysis.

Spin-polarised positive muons were implanted into the δ LFP, δ LFNP(1.0) and δ LFVP(5) samples, where they occupied interstitial sites for a mean lifetime of $2.2\ \mu\text{s}$ before decaying. The muon spin direction was affected by the local magnetic field or diffusing species near the implantation site. The asymmetry in the count rate of the positrons, $A(t)$, was measured in two arrays of detectors on opposite sides of the sample. While the implanted muons are almost 100% polarised, their three-body decay into a positron and two neutrinos, as well detector geometry constraints, limited the positron count rate asymmetry to *ca.* 25% on the EMU instrument. In order to probe the lithium diffusion behaviour in the three samples, measurements were in the temperature range 100 to 400 K for all samples. At each temperature, measurements were made at multiple magnetic fields (applied along the initial muon spin direction). These gave a way of comparing the applied field to the internal fields experienced by muons in the sample and constrained the model used for analysing the data more rigorously than could have been done with a single measurement. The Li^+ diffusion was investigated in this study with μ SR with zero applied field (ZF) and varying strengths of applied longitudinal field (LF) at 5, 10 and 20 G. Representative muon decay asymmetry spectra at 290 K for sample LFP at 0 and 20 G are shown in Fig. 1.

The spectra arose from a combination of a rapid interaction with the paramagnetic iron moments, and a slower interaction with the ^6Li , ^7Li and ^{31}P nuclear magnetic moments. This allowed Li^+ diffusion to be extracted in a similar manner to previous μ SR studies of LiFePO_4 ^{7,8}. The data sets were fitted using four different parameters. Firstly, Keren's analytic generalization of the Abragam function was applied, which has previously been altered to describe fluctuations due to Li^+ or μ^+ diffusion (assuming a Gaussian distribution of local fields)⁷. This function was chosen due to the increased relative speed of computation of the Keren function compared to the Kubo-Toyabe function used in previous studies⁵. Secondly, an exponential relaxing function was used, accounting for the rapid interaction with iron electronic magnetic moments. Thirdly, a baseline asymmetry was used to account for weak interactions with Ti and C present in the sample holder and sample, respectively. Finally, an additional exponentially decaying function was added as a separate term, to account for interactions with minor ferric impurities. These were not observed by XRD, so are assumed to be very minor, or amorphous. By fitting with these parameters, the muon fluctuation rate (ν_{Li}) due to Li^+ diffusion and the local field distribution (Δ), could be extracted.

Results and Discussion

X-Ray diffraction analysis of the δ LFP, δ LFNP(1.0) and δ LFVP(5) samples, confirmed each crystallised in the $Pnma$ space group of the olivine structure (Fig. 2). The high-quality XRD revealed a minor impurity peak in

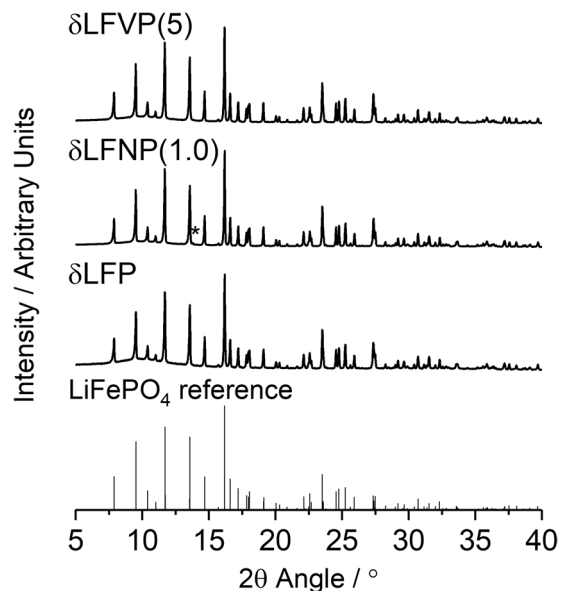


Figure 2. X-Ray diffraction patterns of δ LFP, δ LFP(1.0) and δ LFP(5) with an LiFePO_4 standard (PDF Card No. 01-070-6684), with the $\text{Fe}_2\text{P}_2\text{O}_7$ minor impurity phase peak (PDF Card No. 00-076-1672, present in 1.5 vol% from Rietveld refinement) highlighted with an asterisk. A more detailed figure of the impurity phase peak is shown in Figure S2.

Sample	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$	R_{wp}	χ^2
δ LFP	10.32407 (14)	6.00399 (9)	4.69447 (7)	290.990 (13)	4.48	1.34
δ LFP (1.0)	10.32252 (9)	6.00098 (6)	4.69633 (5)	290.915 (8)	3.79	2.20
δ LFP (5)	10.32345 (9)	6.00260 (6)	4.69687 (5)	291.054 (8)	3.84	2.21

Table 1. The lattice parameters and goodness-of-fit parameters calculated from Rietveld refinement.

δ LFP(1.0) (at $2\theta \sim 13.8^\circ$), which is consistent with $\text{Fe}_2\text{P}_2\text{O}_7$ and has been observed previously in heat-treated carbon-coated olivines (Figure S2)²⁷. The lattice parameters were extracted from Rietveld analysis using MAUD (Material Analysis Using Diffraction) software²⁸, and are displayed in Table 1 and plots of the refinements are displayed in Figures S3–S5. The dopants had a minor effect on the lattice parameters, with a small contraction of the b -axis and lengthening of the c -axis, consistent with previous studies of doped samples^{20,21}. This crystallographic change is primarily due to the different ionic radii of V^{3+} (0.64 Å) and Nb^{5+} (0.64 Å) occupying the Fe^{2+} (0.78 Å) site. Occupation of V on the Fe site with a Li vacancy as a charge-compensation mechanism in LiFePO_4 was confirmed by the authors previously for δ LFP(5) with a combined Extended X-Ray Absorption Spectroscopy (EXAFS) and Density Functional Theory (DFT) study²¹, with the V:Fe ratio quantified as 5:95 by ICP-AES analysis. In addition, the authors confirmed an even dispersion of Nb within Nb-doped LiFePO_4 samples²³, with no Nb-containing impurity phases observed. The proportion of Nb within LiFePO_4 was found to approximately match the stoichiometry of the precursors (Figures S6 and S7).

The behaviour of Δ was similar to that reported previously by others for undoped LiFePO_4 , i.e. a steady decrease with increasing temperature, although the values for Δ were consistently lower for the doped samples (Fig. 3). The relative reduction in Δ seen in the doped samples herein cannot be definitively attributed, but could originate from an altered occupation of muon stopping sites, increased Li vacancies or changes in the muon mobility within the sample.

All samples showed a characteristic increase and then decrease in ν_{Li} with temperature, although the magnitude of ν_{Li} was about 10% of that reported in the literature for undoped LiFePO_4 samples previously (Fig. 4a–c)^{6–8}. This may have been due to the significant embedding of muons in the carbon shell (range of 3 to 9 wt% carbon within the three samples, Table S1, corresponding to 1:2 and 1:1 molar ratios of C: LiFePO_4), which would have detracted from the overall measured diffusion rate, but would not be expected to contribute to the observed fluctuation rate. For δ LFP and δ LFP(1.0), an increase in ν_{Li} with increasing T in the range ca. 180–250 K and a decrease thereafter was observed (Fig. 4a,b). In contrast, δ LFP(5) displayed a rapid increase of ν_{Li} in the range 170–210 K, followed by a rapid decay above 210 K to a lower value of ν_{Li} (0.03 MHz, Fig. 4c). This behaviour indicated there may be some observable difference in diffusion behaviour of δ LFP(5) and the other samples in this temperature range. However, given the relative error of the data points, further experiments are necessary to confirm the existence of any deviation from normal diffusion behaviour in vanadium-doped LiFePO_4 .

The hopping rate of Li^+ can be converted to a diffusion coefficient according to Equation 1, where N_i is the number of Li sites in the i th path, Z_{vi} is the vacancy fraction, and s_i is the hopping distance²⁹. Therefore, as Li can

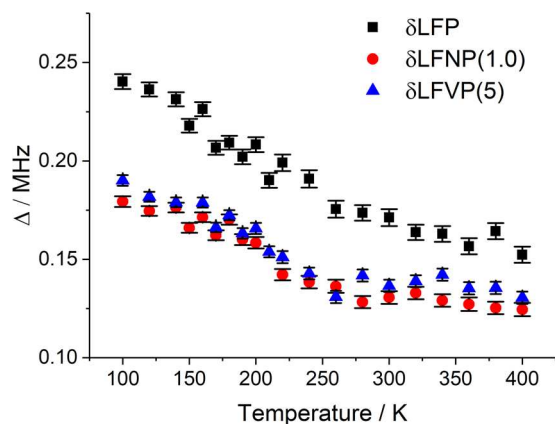


Figure 3. The local field distribution (with error bars) as a function of temperature for samples δ LFP, δ LFNP(1.0) and δ LFVP(5).

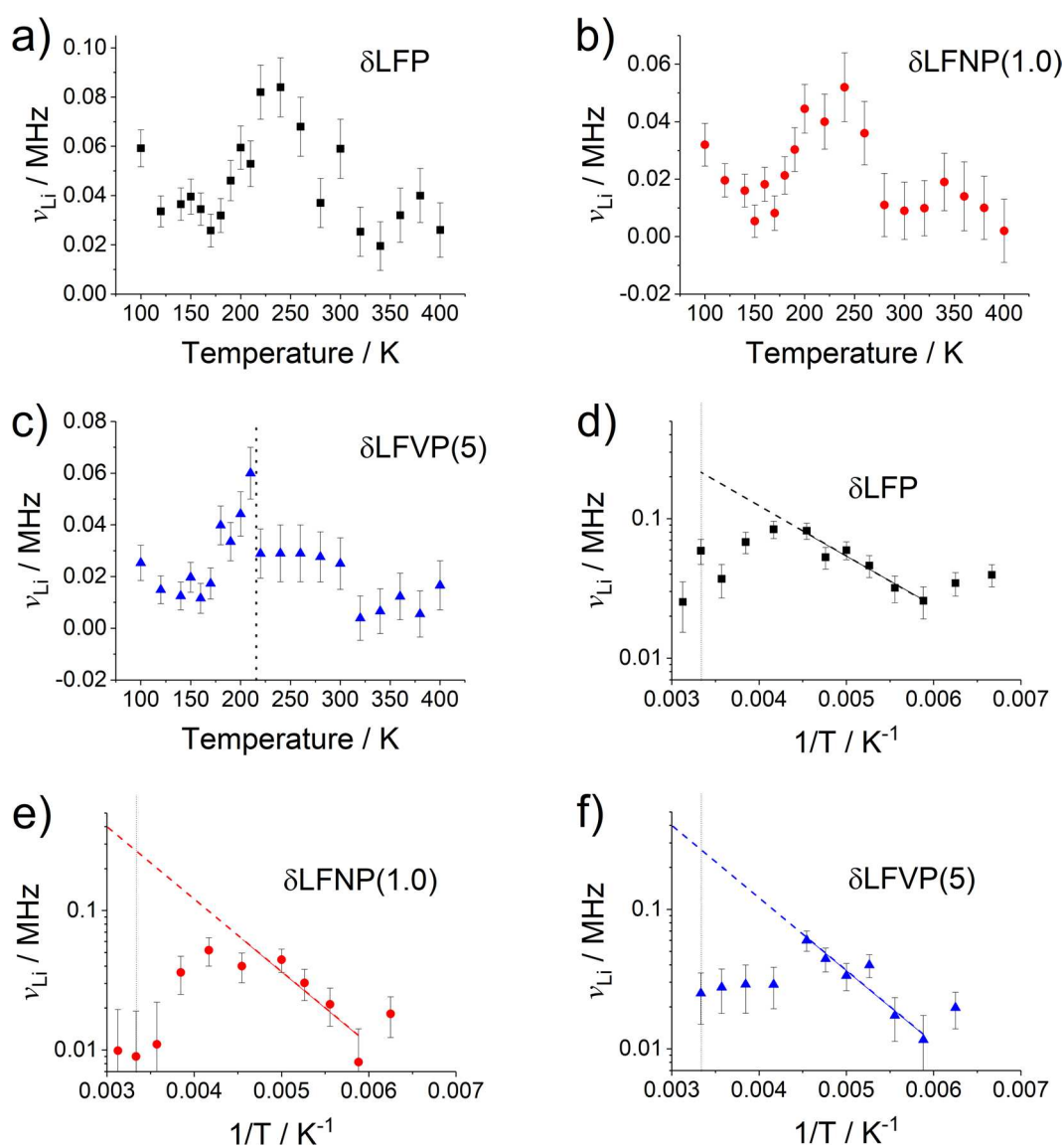


Figure 4. Plots of muon fluctuation rates ν_{Li} vs Temperature for (a) δ LFP, (b) δ LFNP(1.0) and (c) δ LFVP(5). Extrapolations of the muon fluctuation rate ν_{Li} to room temperature on a log plot (indicated by the dotted line) vs inverse temperature ($1/T$) for (d) δ LFP, (e) δ LFNP(1.0) and (f) δ LFVP(5).

Sample	$D_{\text{Li}} @ 300 \text{ K/cm}^2 \text{ s}^{-1}$	E_a/meV
δLFP	$1.8 \pm 2 \times 10^{-10}$	70 ± 10
$\delta\text{LFNP (1.0)}$	$2.1 \pm 20 \times 10^{-10}$	100 ± 18
$\delta\text{LFVP (5)}$	$2.3 \pm 6 \times 10^{-10}$	100 ± 30

Table 2. The calculated diffusion coefficients and gradients from μSR .

diffuse in either direction along the 1D LiFePO_4 diffusion tunnels, $n = 2$, where the number of vacant sites in each direction is 1, i.e. $N_1 = N_2 = 1$. For diffusion to occur, there must be a vacancy in the neighbouring sites, so $Z_1 = Z_2 = 1$. Therefore, Equation 1 simplifies to Equation 2. As Li^+ diffusion in LiFePO_4 has been shown to occur exclusively along the b -axis³⁰, the hopping length is approximately $b/2$, and therefore D_{Li} can be estimated from $b^2 v_{\text{Li}}/4$, and extrapolating v_{Li} against $1/T$ can determine a value for the Li-ion diffusion coefficient at room temperature (Fig. 4d–f). As the carbon coating contains no mobile lithium, it was assumed that the diffusion distance was accurately described by $b/2$.

$$D_{\text{Li}} = \sum_{i=1}^n \left(\frac{1}{N_i} Z_{v,i} s_i^2 v_{\text{Li}} \right) \quad (1)$$

$$D_{\text{Li}} = s_i^2 v_{\text{Li}} \quad (2)$$

Diffusion coefficients of approximately $2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ were estimated for δLFP , $\delta\text{LFNP(1.0)}$ and $\delta\text{LFVP(5)}$, respectively, which were similar within error (Table 2). As a comparison, the diffusion coefficient values obtained here were consistent with those obtained by μSR for undoped LiFePO_4 previously, pointing to the reliability of this technique for determining the diffusion properties of off-stoichiometry olivines^{5,7,8}. The activation energies of Li^+ diffusion (calculated from the gradient of diffusion coefficient against $1/T$) were also consistent with previous analyses; E_a was in the range 70–100 meV for all samples^{5,7,8}. For example, Baker *et al.* found D_{Li} values in the range $4\text{--}20 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and E_a values in the range 80–130 meV for the lithium-deficient olivines, $\text{Li}_{1-x}\text{FePO}_4$ (where $0 \leq x \leq 0.2$)⁷. Indeed, Baker *et al.* found greater values of E_a for their Li-deficient samples, which suggests that Li deficiencies present in doped LiFePO_4 (Table S2) may be responsible for any difference observed between samples in the temperature range 170–210 K. However, no quantitative difference in diffusion coefficient was observed between the undoped and doped samples when the low-temperature data was extrapolated to room temperature. This suggested that the intrinsic Li^+ diffusion hopping rate at room temperature was not affected by doping, and that any enhancement of electrochemical performance observed must be due to other factors, such as increased electronic conductivity, or stabilisation of the $\text{Li}_{1-x}\text{FePO}_4$ and Li_xFePO_4 solid solutions. Such an observation could not be made via conventional techniques, such as impedance spectroscopy, as the two-phase delithiation mechanism of LiFePO_4 prevents accurate probing of Li^+ diffusion.

Conclusions

Li^+ diffusion within V- and Nb-doped LiFePO_4 samples, made *via* a continuous hydrothermal process³¹, have been characterised with muon spectroscopy for the first time. The calculated Li^+ diffusion coefficients were close to the values previously reported for bulk and nanometric undoped LiFePO_4 . Thus, this report highlights the versatility of the μSR technique to analyse families of materials made by a variety of synthesis techniques. Within experimental error, the Li^+ diffusion data suggested that electrochemical enhancements due to doping are not a result of improved local Li^+ diffusion. Rather, the authors suggest that other factors, such as increased electronic conductivity or stabilisation of the $\text{Li}_{1-x}\text{FePO}_4$ and Li_xFePO_4 solid solutions may account for these enhancements. Therefore, these results have indicated the utility of μSR to provide key insights into the diffusive behaviour of doped LiFePO_4 , and could be applied to further battery materials in the future.

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Author Contributions

IDJ wrote the paper, performed the synthesis and XRD characterisation, with EB assisting with the latter. IDJ, TEA, GJS and PJB collected and fitted the muon data. ML and SAC contributed to the discussion and editing of the manuscript. JAD is the supervising scientist of the research team at University College London and co-developed the synthesis technology for the nanomaterials that were measured herein.

Additional Information

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