Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information for:

Particle Size Dependent Confinement and Lattice Strain Effects in $LiFePO_4$

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In the following supplementary section, we report the complex impedance spectra of representative two different particle size of LFP in Nyquist plot (figure S1) and an estimated hopping length (figure S2) of LFP with different particle sizes using the Mott equation. In addition, we also report the x-ray diffraction analysis and Rietvield refinement procedure adopted in the present investigation on $LiFePO_4$ for representative two different particle sizes (figure S3 and S4).

Representation of Impedance of $LiFePO_4$ samples in Nyquist plot

In figure S1 ((a) and (b)), we show the representative impedance spectra measured at three different temperatures for 50 nm and 1000 nm particle sizes of LFP. It is clear from the Nyquist plot that only one semicircle has been observed and it corresponds to the bulk component of LFP and we discard any grain boundary contributions in the present investigation. Furthermore, we represent the estimated hopping length of polarons for different particle sizes in figure S2, where it decreases significantly while reducing the particle size from bulk into nanoscale.

XRD and Rietvield refinement procedure:

X-ray powder diffraction patterns of all the LFP samples were collected with a Panalytical Empyrean using Cu Kα radiation and equipped with PIXcel detector operating at 40kV-30mA in the range 2θ=15°-70° with a 2θ step size of 0.013°. Rietvield refinements were carried out by using TOPAS software. The refinements

were conducted by taking initial cell parameters and atomic positions as those reported by Wagemaker *et.al* .[1] The fitting was done for the whole data set collected in 2θ range from 15° to 70° and by starting with Le bail fit in which nominal LFP parameters were inserted without providing atomic coordinates and occupancy factor. After Le bail converged to satisfactory limit, proper Rietvield analysis was started providing all atomic parameters along with occupancy factor. However during first stage all these parameters were kept close those reported by Wagemaker and all occupancies were constrained to ideal value of unity. To improve the fit, Li and Fe occupancies were allowed to vary and the value obtained in each case was used as a constraint for further refinements. An improvement in the fit was observed when simultaneous presence of Fe and Li on M1 site keeping the constrained Fe occupancy value. Finally Li occupancy was left to vary along with Fe occupancies. Other elements occupancies were fixed to their nominal value. In all the cases temperature factors were kept to isotropic mode. The lattice parameters, reliability factors and atomic coordinates obtained are listed in table 1 - 4 for 1000nm and 50nm particles along with their Rietvield refined pattern in figure S2 and figure S3 respectively.

[1] M. Wagemaker et.al. *Chem. Mater.*, 2008**, 20**, 6313-6315.

XRD Rietveld refinement results for sample 1000 nm

Table 1. Lattice constants and Rietveld refinement results for LFP sample with 1000 nm	
Wavelength (Å)	1.5405
Space group (No.)	Pnma(62)
a (Å)	10.33572
b (Å)	6.01245
c (Å)	4.69762
V ($Å^3$)	291.92412
R_p (%)	3.58
R_{wp} (%)	4.63
R_{exp} (%)	3.76
GoF (χ^2)	1.23

Table 2. Atomic coordinates of LFP sample with 1000 nm

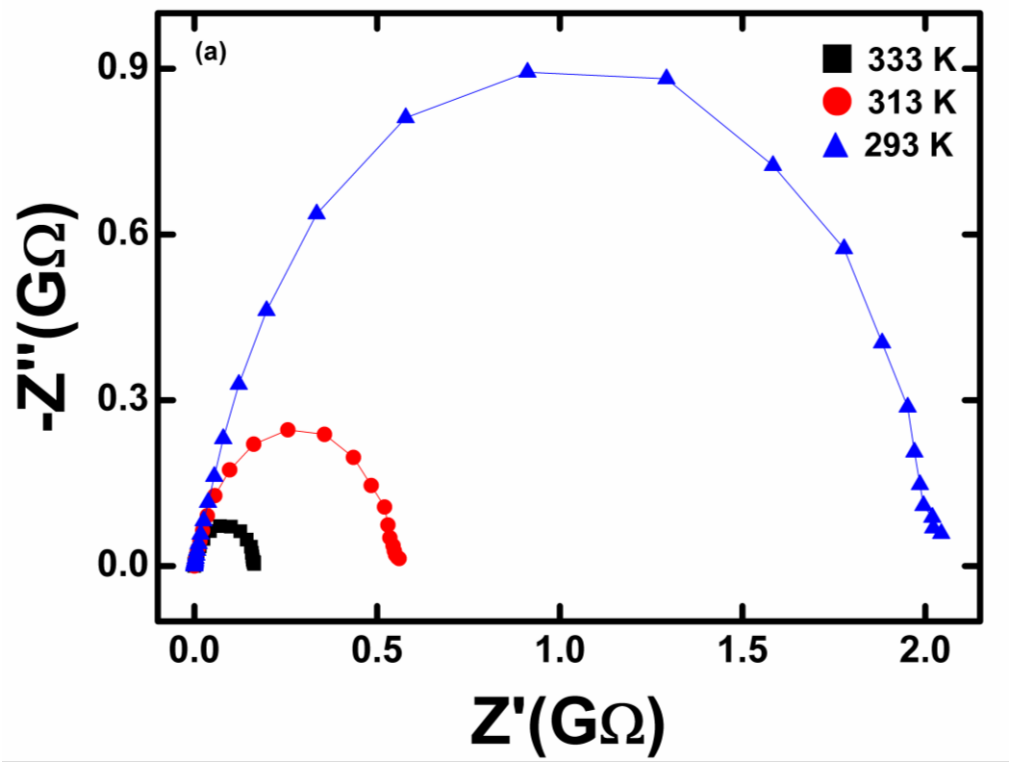
Site	Wyck.	x/a	y/b	z/c	S.O.F	B_{iso}
Li	4a	0.00000	0.00000	0.00000	0.9992	0
Fe	4c	0.28145	0.25000	0.97455	0.9997	0
P	4c	0.09449	0.25000	0.41288	1	0
O(1)	4c	0.09527	0.25000	0.73948	1	0
O(2)	4c	0.45450	0.25000	0.21060	1	0
O(3)	8d	0.17098	0.03750	0.27904	1	0
Fe	4a	0.00000	0.00000	0.00000	0.00059	0

XRD Rietveld refinement results for sample 50 nm

Table 3. Lattice constants and Rietveld refinement results for LFP sample with 50 nm	
Wavelength (Å)	1.5405
Space group (no.)	Pnma(62)
a (Å)	10.29583
b (Å)	5.99068
c (Å)	4.70182
V ($Å^3$)	290.00345
R_p (%)	2.39
R_{wp} (%)	3.43
R_{exp} (%)	1.67
GoF (χ^2)	2.05

Table 4. Atomic coordinates of LFP sample with 50 nm

Site	Wyck.	x/a	y/b	z/c	S.O.F	B_{iso}
Li	4a	0.00000	0.00000	0.00000	0.8054	0
Fe	4c	0.28079	0.25000	0.97510	0.9381	0
P	4c	0.09587	0.25000	0.40964	1	0
O(1)	4c	0.09226	0.25000	0.73299	1	0
O(2)	4c	0.45051	0.25000	0.19476	1	0
O(3)	8d	0.16326	0.04415	0.27974	1	0
Fe	4a	0.00000	0.00000	0.00000	0.0591	0



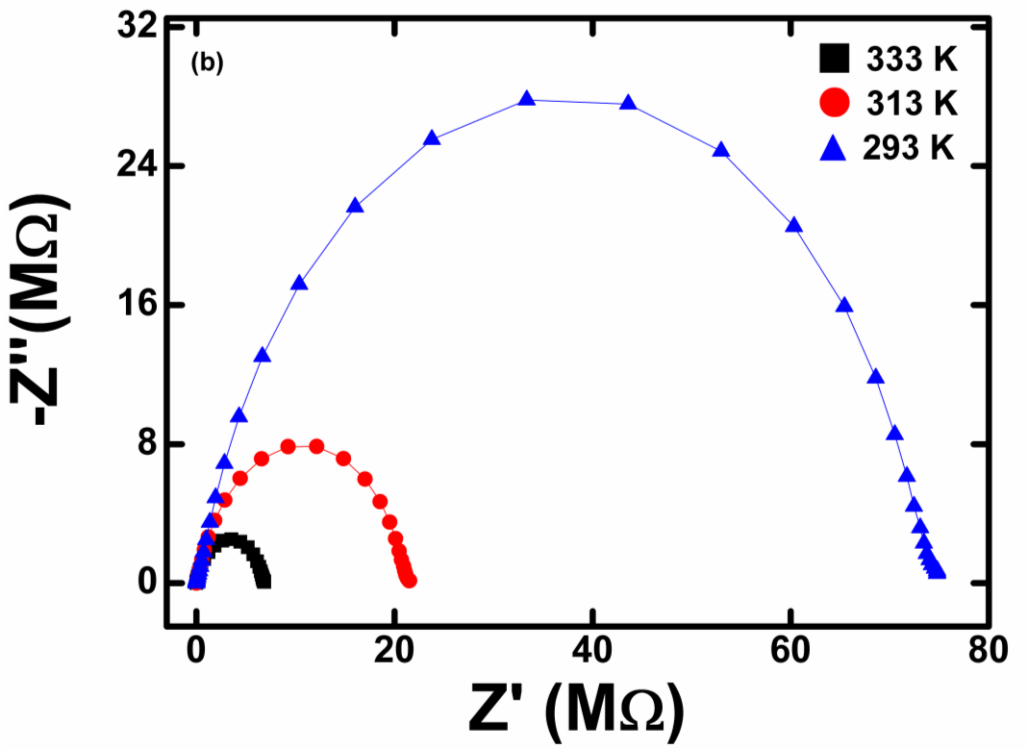


FIG. S1 Complex impedance plots of $LiFePO_4$ sample at different temperatures for

(a) 1000 nm and (b) 50 nm particle sizes.

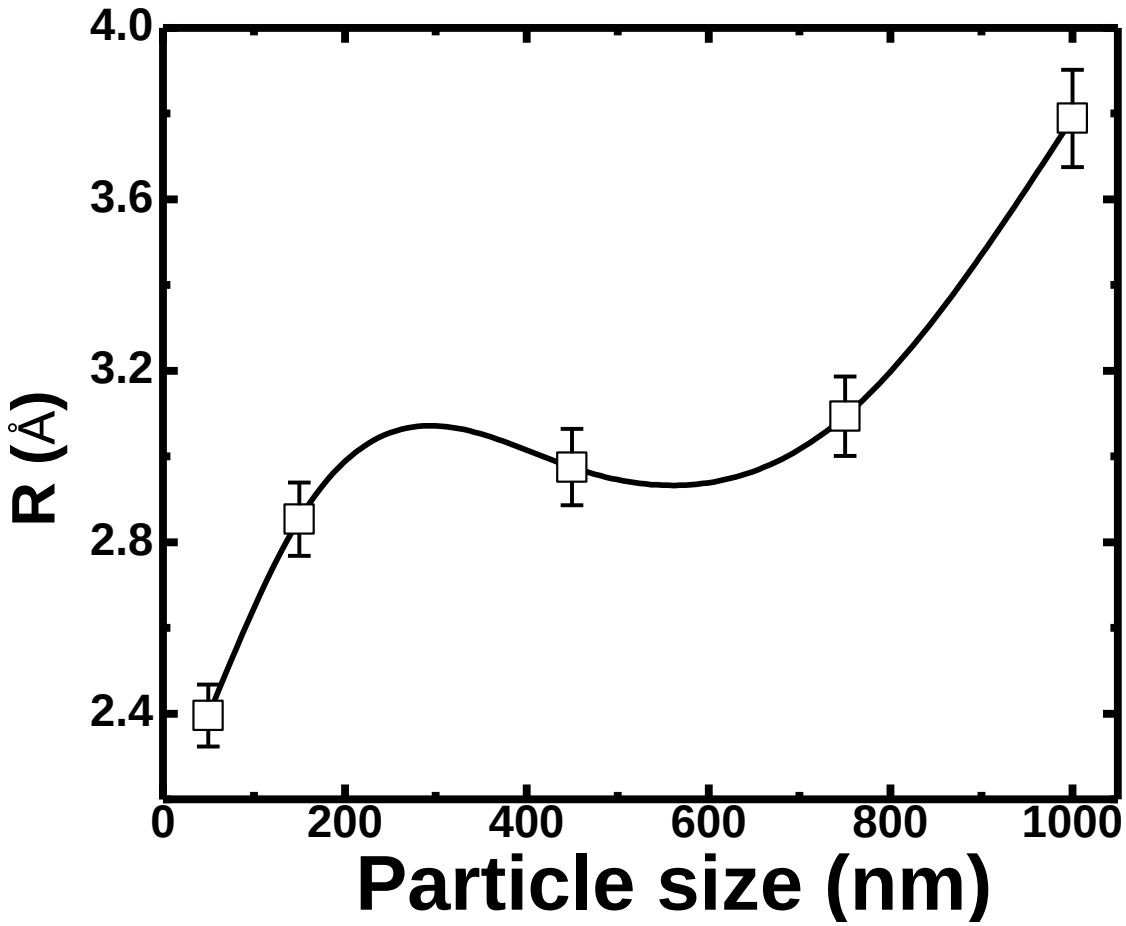


FIG. S2 The estimated hopping length of polaron by using the Mott equation for different particle size of $LiFePO_4$.

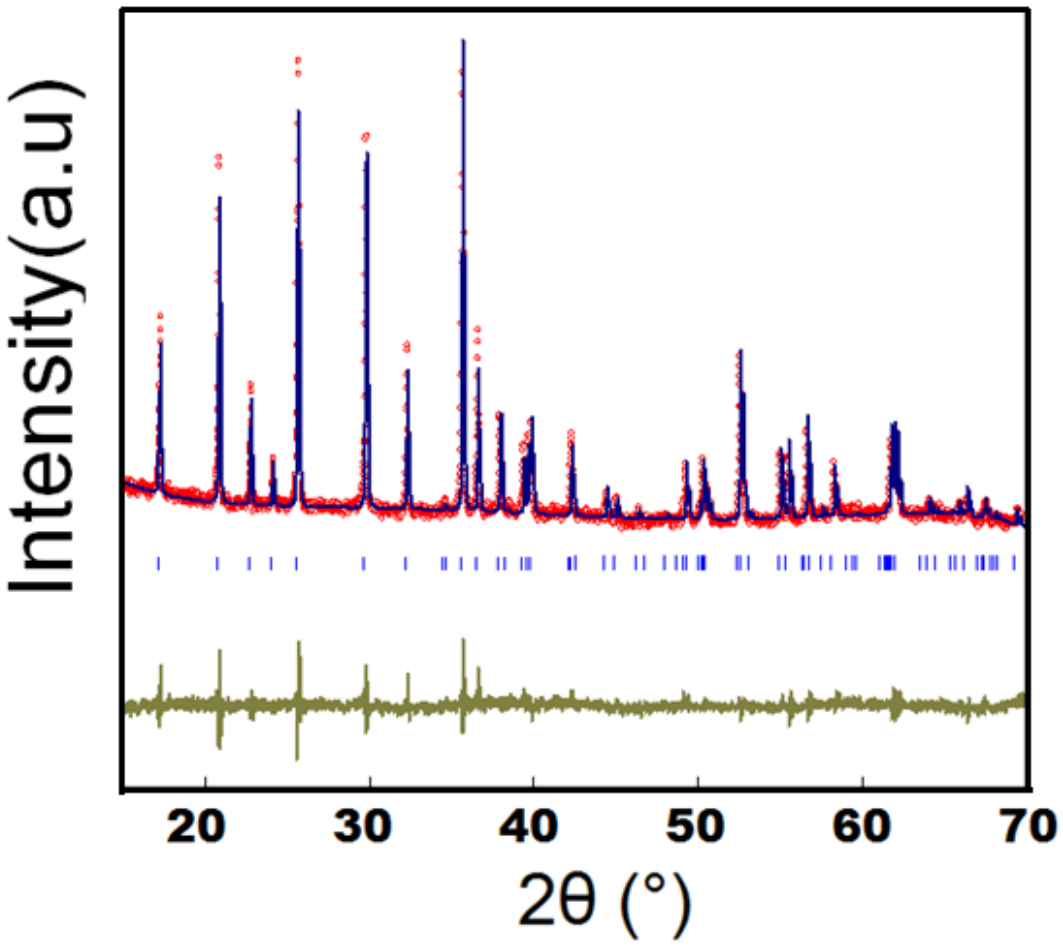


FIG. S3 Experimental X-ray powder diffraction pattern (open circle with red colour) of $LiFePO_4$ with 1000nm sample of compared to the Rietvield refine profile (continuous blue line) and the difference curve (bottom curve) taken at room temperature. The vertical markers (blue) below the diffraction pattern indicate positions of possible Bragg reflections.

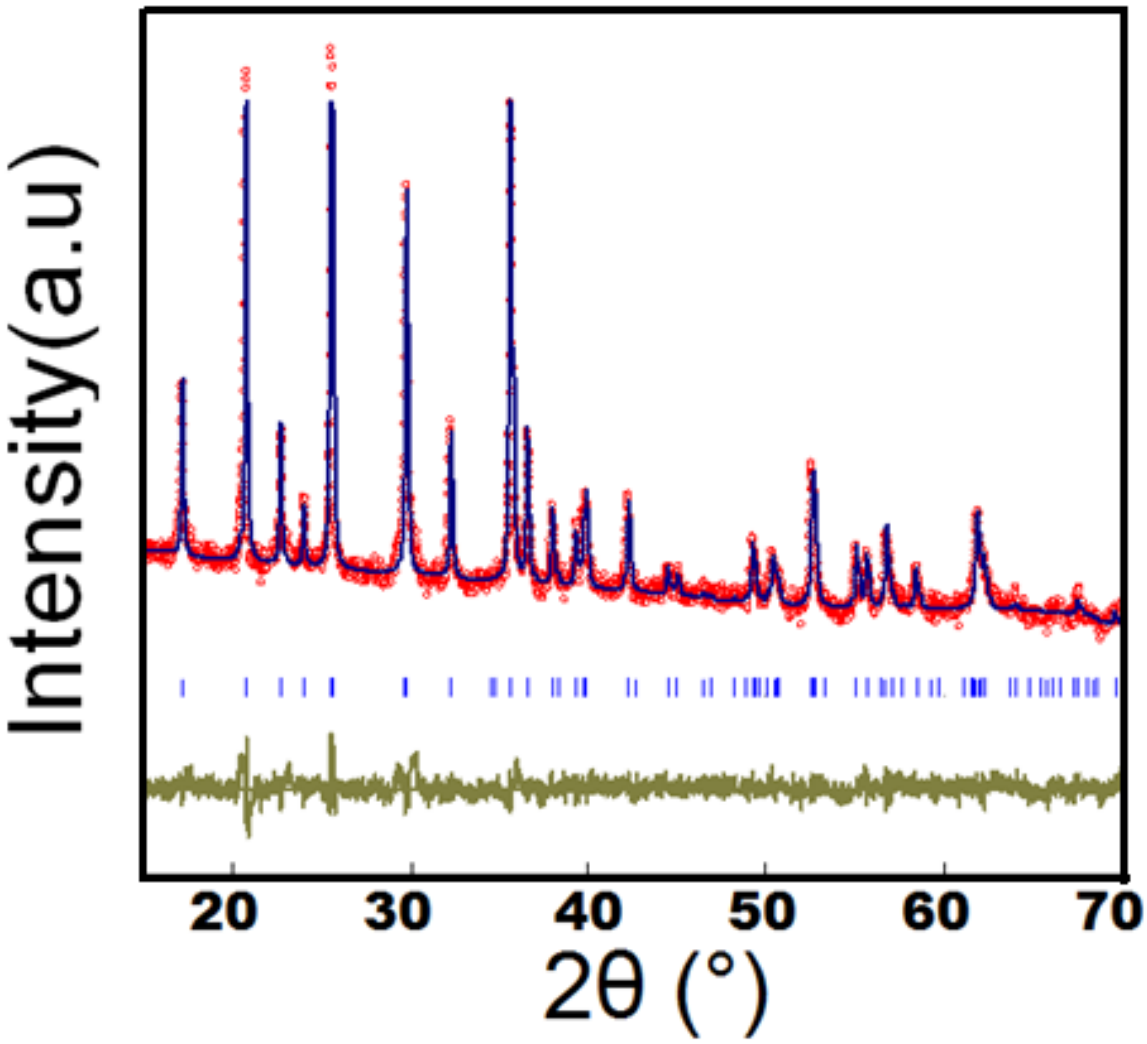


FIG. S4 Experimental X-ray powder diffraction pattern (open circle with red colour) of $LiFePO_4$ with 50nm sample of compared to the Rietvield refine profile (continuous blue line) and the difference curve (bottom curve) taken at room temperature. The vertical markers (blue) below the diffraction pattern indicate positions of possible Bragg reflections.