Electronic Supplementary Information (ESI):

Effect of Strain on Electronic Structure and Polaronic Conductivity in $LiFePO_4$

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Table TS1. Synthesis conditions adopted for synthesizing $LiFePO_4$ samples

Specimen Code	Temperature (K)	Calcination duration (hr)
S1	1023	15
S2	973	12
S3	1023	06

Table TS2. Rietveld refinement parameters of LFP sample

Specimen Code			S1		
Wavelength			0.7177 Aº		
Space group			*Pnma*		
Lattice parameter					
a (Aº)		b (Aº)		c (Aº)	
10.3397 ± 0.0002		6.0127 ± 0.0001		4.6956 ± 0.0001	
Volume (A^3)			291.925 ± 0.009		
Li^+ Vacancy (%)			1.06%		
R_p (%)			3.86%		
R_{wp} (%)			5.34%		
GOF (χ^2)			4.823		
Site	Wyckoff Positions	x/a	y/b	z/c	Occupancy
Li	4a	0.0000	0.0000	0.0000	0.9894
Fe	4c	0.2821	0.25	0.9742	0.9661
Fe	4a	0.0000	0.0000	0.0000	0.0037
P	4c	0.0957	0.25	0.4168	1.0000
O	4c	0.0969	0.2500	0.7443	1.0000
O	4c	0.4544	0.2500	0.2156	1.0000
O	8d	0.1666	0.0465	0.2795	1.0000

Specimen code			S2		
Wavelength Space group			0.7134 Aº *Pnma*		
Lattice parameter					
a (Aº)		b (Aº)		c (Aº)	
10.3553 ± 0.0002		6.0226 ± 0.0001		4.7026 ± 0.0001	
Volume (A^3) Li^+ Vacancy (%) R_p (%) R_{wp} (%) GOF (χ^2)			293.284 ± 0.006 0.3 % 3.07% 4.36% 2.994		
Site	Wyckoff Positions	x/a	y/b	z/c	Occupancy
Li	4a	0.0000	0.0000	0.0000	0.9970
Fe	4c	0.28183(8)	0.2500	0.9739(26)	0.9984
Fe	4a	0.0000	0.0000	0.0000	0.0017
P	4c	0.09480(19)	0.2500	0.4172(4)	1.0000
O	4c	0.0962(4)	0.2500	0.7436(7)	1.0000
O	4c	0.4561(5)	0.2500	0.2094(7)	1.0000
O	8d	0.1669(34)	0.0456(5)	0.2852(5)	1.0000

Specimen Code			S3		
Wavelength Space group			0.7134 Aº *Pnma*		
Lattice parameter					
a (Aº)		b (Aº)		c (Aº)	
10.3538 ± 0.0002		6.0204 ± 0.0002		4.7063 ± 0.0001	
Volume (A^3) Li^+ Vacancy (%) R_p (%) R_{wp} (%) GOF (χ^2)			293.100 ± 0.008 1.54 % 3.27% 4.46% 3.809		
Site	Wyckoff Positions	x/a	y/b	z/c	Occupancy
Li	4a	0.0000	0.0000	0.0000	0.9846
Fe	4c	0.2827	0.2500	0.9737	0.9996
Fe	4a	0.0000	0.0000	0.0000	0.0000
P	4c	0.2803	0.2500	0.9766	1.0000
O	4c	0.0953	0.2500	0.4160	1.0000
O	4c	0.4564	0.2500	0.2087	1.0000
O	8d	0.1651	0.0464	0.2836	1.0000

Table TS3. Interatomic distances and bond angels evaluated from the Rietveld refinement

	S1	S2	S3
	Fe-Octahedron		
Fe-O (1)	1 x 2.19875(5)	1 x 2.206(4)	1 x 2.223(5)
Fe-O (2)	1 x 2.11162(4)	1 x 2.117(5)	1 x 2.112(5)
Fe-O (3)	2 x 2.07274(4)	2 x 2.0607(29)	2 x 2.0675(32)
Fe-O (3')	2 x 2.23098(4)	2 x 2.2508(27)	2 x 2.2594(30)
Average Fe-O Bond	2.1529	2.1576	2.1648
	Li- Octahedron		
Li-O (1)	2 x 2.16890(4)	2 x 2.1709(27)	2 x 2.1908(32)
Li-O (2)	2 x 2.06518(4)	2 x 2.0827(25)	2 x 2.0847(28)
Li-O (3)	2 x 2.18363(4)	2 x 2.2034(33)	2 x 2.188(4)
Average Li-O	2.13923	2.15233	2.1545
	P Tetrahedron		
P-O (1)	1 x 1.53812(4)	1 x 1.5365(32)	1 x 1.508(4)
P-O (2)	1 x 1.58714(4)	1 x 1.555(5)	1 x 1.551(6)
P-O (3)	2 x 1.56528(3)	2 x 1.5682(32)	2 x 1.5537(35)
Average P-O Bond	1.563955	1.5569	1.5416
	Bond angle		
O (1)-Fe-O (2)	177.984(0)	177.83(14)	180.000(1)

Table TS4. The isomer shift (δ), quadrupole splitting (ΔE_Q: doublet), outer line-width (Γ) and relative areas (R_A) in percentage of different sites of Fe^{3+} or Fe^{2+} ions for all five samples derived from Mössbauer spectra recorded at room temperature. Isomer shift values are relative to Fe metal foil (δ = 0.0 mms^{-1}). χ^2: goodness of fit.

Specimen Code	**Iron Sites**	δ **(mms^{-1})**	ΔE_Q **(mms^{-1})**	Γ **(mms^{-1})**	R_A **(%)**	χ^2
S1	Doublet-A Fe^{2+}	1.2485	2.9914	0.3556	92.82%	1.50
	Doublet-B Fe^{3+}	0.4772	0.6309	0.3912	7.18%	
S2	Doublet-A Fe^{2+}	1.2353	2.9882	0.3746	96.30%	0.89
	Doublet-B Fe^{3+}	0.4367	0.7580	0.3947	3.70%	
S3	Doublet-A Fe^{2+}	1.2543	2.9914	0.3603	99.22%	1.35
	Doublet-B Fe^{3+}	0.4203	0.8621	0.3933	0.78%	

Table TS5. Simulated parameters for D_{4h} symmetry for the different LFP samples

Specimen Code	10Dq(eV) (Fe L edge)	D_s(eV)	D_t(eV)	Δt_{2g}(eV) ($3D_s$-$5D_t$)	Δe_g (eV) ($3D_s$ + $5D_t$)
S1	1	0.48	0.05	1.19	1.69
S2	0.9	0.52	0.01	1.51	1.61
S3	1.1	0.48	0.06	1.14	1.74

Table TS5: Fe 3d orbital energies in LFP with D_{4h} symmetry calculated for different micro strain samples.

Specimen Code	b_{1g} (eV)	a_{1g} (eV)	b_{2g} (eV)	e_g (eV)
S1	1.51	-0.66	0.51	-1.13
S2	1.57	-0.56	0.67	-0.84
S3	1.56	-0.66	0.46	-0.68

Table TS7. Important Mott parameters related to electronic dc conductivity estimated by the Mott model.

Specimen Code	ν_{ph} (Hz) 10^{13}	E_a^{HT} (eV)	E_a^{IT} (eV)	E_a^{LT} (eV)	Polaron Concentration	Coupling Constant	$\sigma_{(dc)}$ (Scm^{-1}) at 303K
S1	1.12	0.661 ±0.012	0.563 ±0.014	0.470 ±0.019	0.0071	14.35	$3.216*10^{-8}$
S2	2.25	0.642 ±0.013	0.547 ±0.011	0.468 ±0.018	0.006	13.98	$4.206*10^{-8}$
S3	1.56	0.506 ±0.017	0.465 ±0.004	0.414 ±0.0004	0.019	11.89	$1.242*10^{-7}$

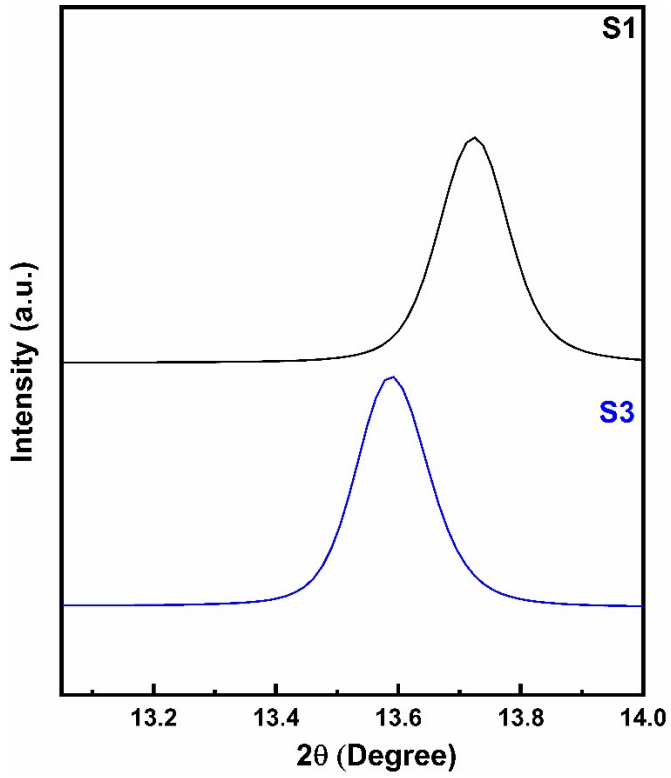

Figure S1. Magnified (211/020) diffraction peak showing broadening and shift towards lower angle with increasing strain

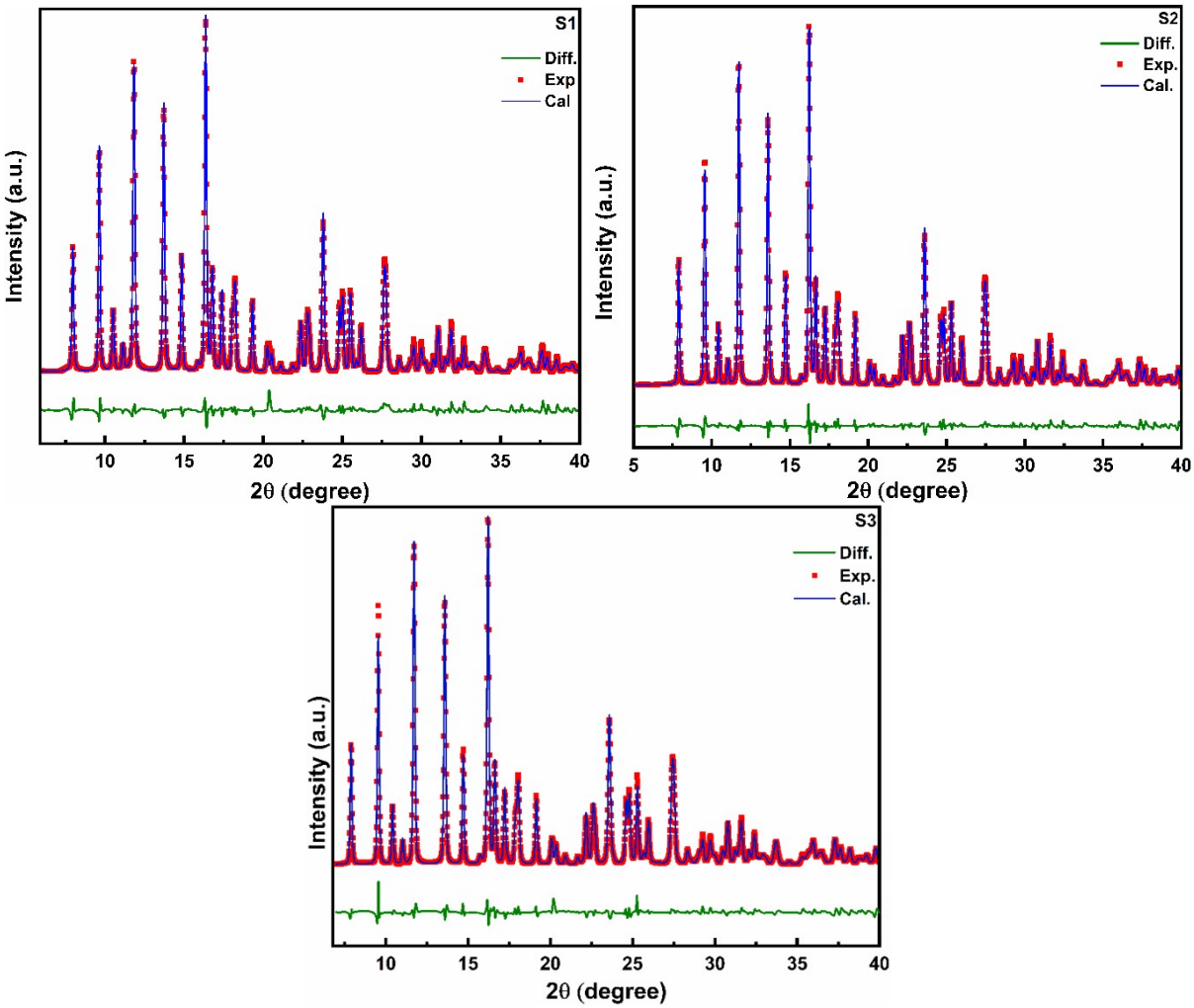

Figure S2. Experimental HRXRD pattern (squares in red color) of $LiFePO_4$, compared with theoretical line profile by Rietveld Refinement (continuous line in blue color), a difference of experimental and theoretical curve is represented by the continuous line in green color. Vertical markers in pink color indicate Bragg's reflection for orthorhombic $LiFePO_4$

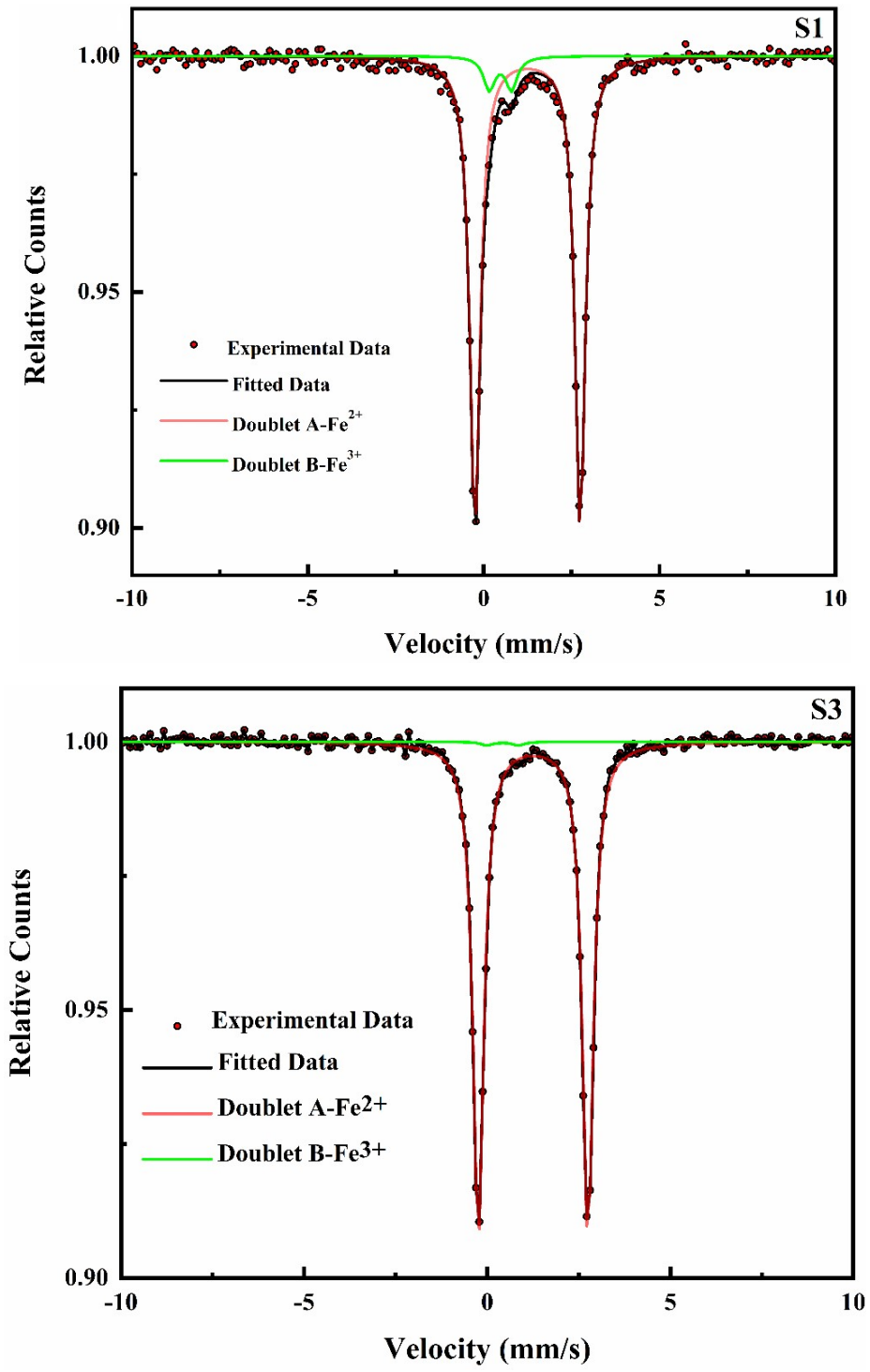

Fig. S3. Fitted ^{57}Fe Mossbauer spectra along with experimental spectra for S1 and S2 specimens. The red-filled circles represent the experimental data and the black solid line indicates the fitted spectra. The green and red solid lines correspond to the contributions from the predominant Fe^{2+} and the trace Fe^{3+} species, respectively.

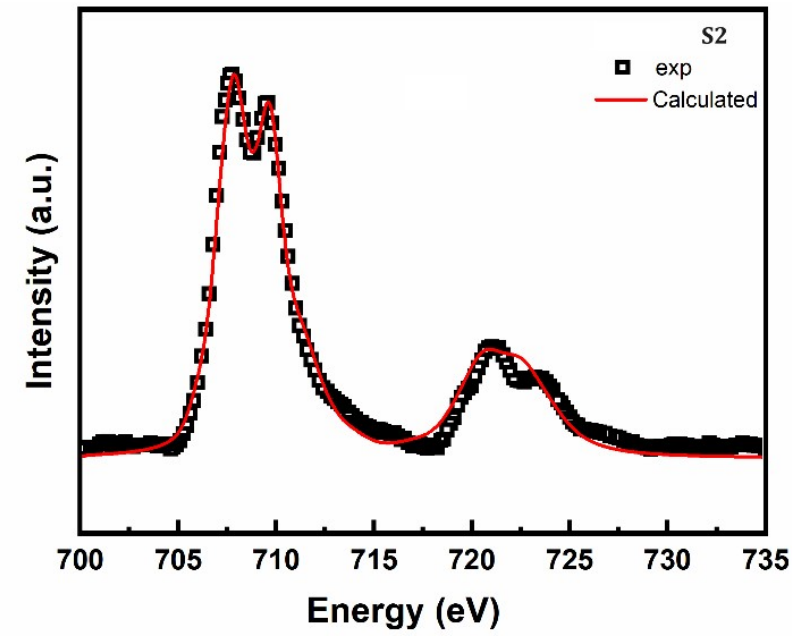

Figure S4. Simulated Fe L edge XAS spectra along with the experimental spectra. Square symbol represents the experimental spectra of S2 LFP specimen and solid red line represents the simulated spectra with the CTM4XAS software

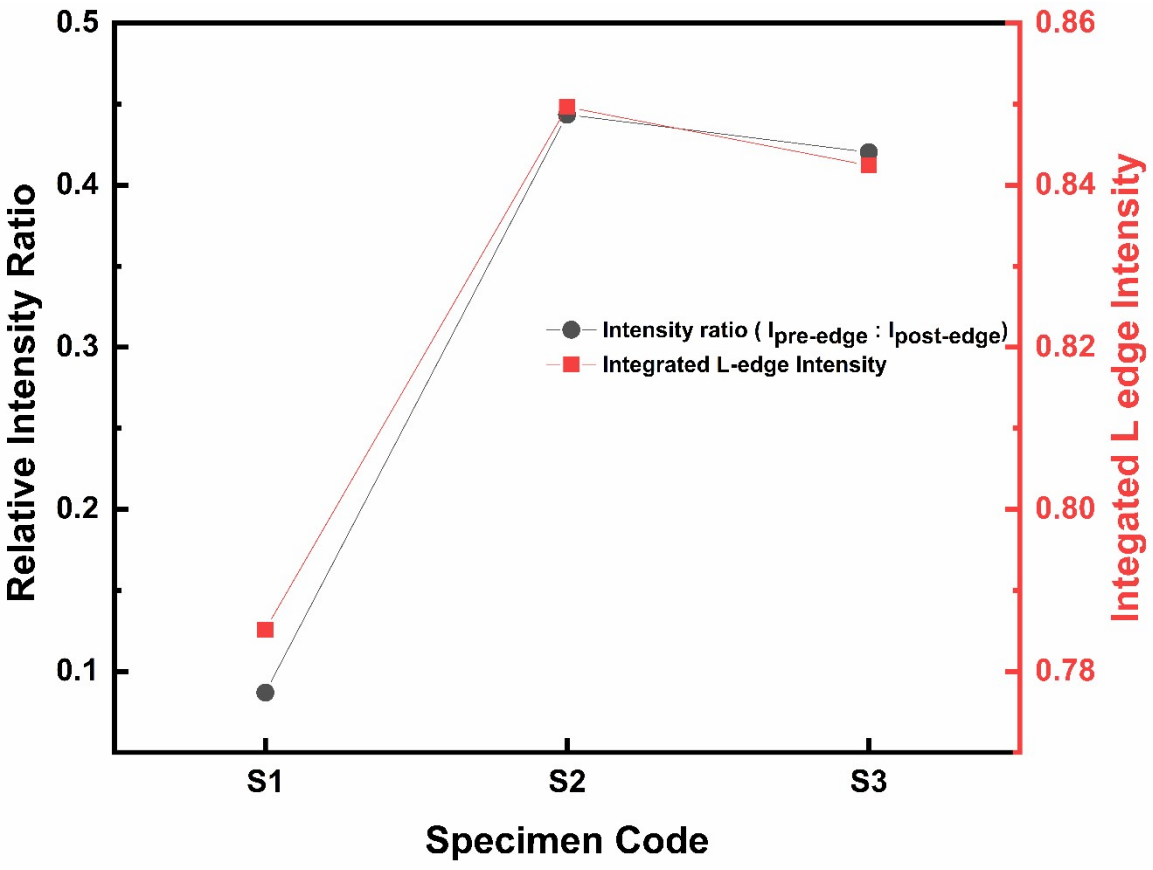

Figure S5. The variation of intensity ratio of pre-edge to post-edge of the O k edge and integrated Fe L edge intensity of XAS spectra for different specimens

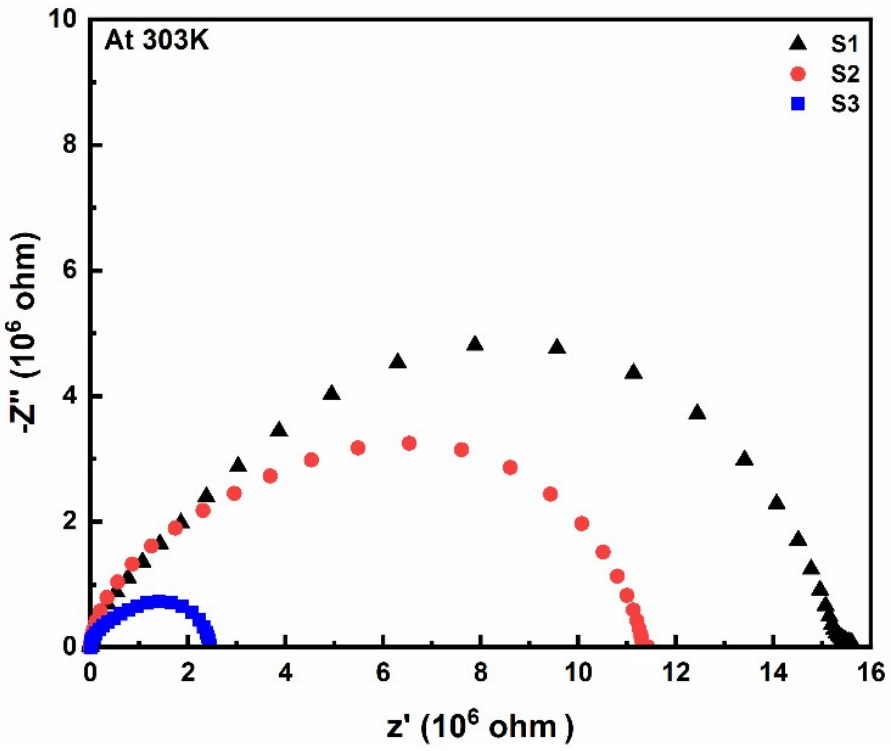

Figure S6. Nyquist plot of different LFP samples at 303 K.

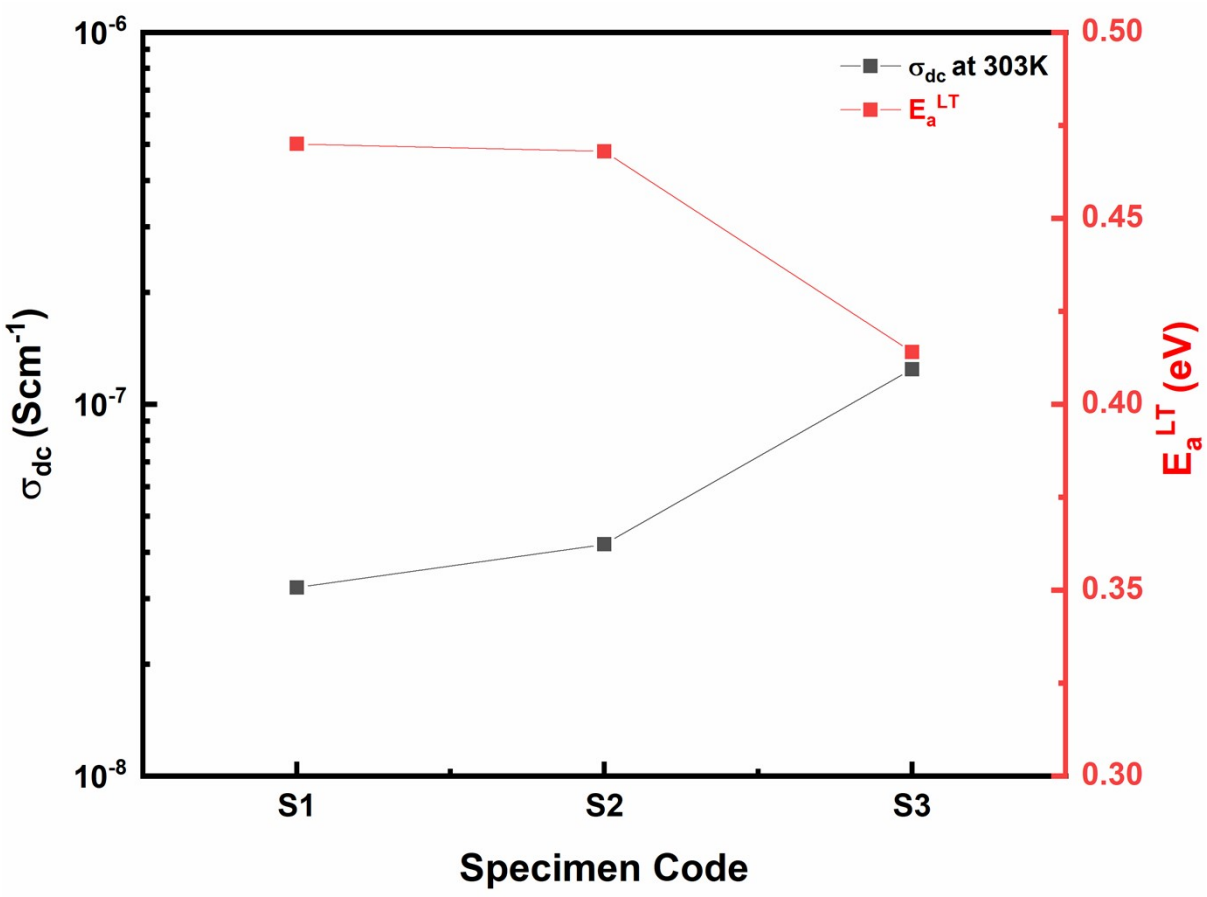

Figure S7. The variation of dc conductivity, $\sigma_{(dc)}$ and activation energy (LT) for different specimens.