Electronic Supplementary Material (ESI) for Faraday Discussions.

A Combined ^{7}Li NMR, Density Functional Theory and Operando Synchrotron X-Ray Powder Diffraction to Investigate a Structural Evolution of Cathode Material $LiFeV_2O_7$

SUPPORTING INFORMATION

Taiana L. E. Pereira[1], Jon Serrano Sevillano[2,3], Beatriz D. Moreno[4], Joel W. Reid[4], Dany Carlier[4] and Gillian R. Goward[4]*

[1]Department of Chemistry & Chemical Biology, McMaster University, 1280 Main St. West, Hamilton, Ontario L8S 4M1, Canada

[2] Centro de Investigación Cooperativa de Energías Alternativas (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), 01510 Vitoria-Gasteiz, Spain.

[3]CNRS, Bordeaux INP, ICMCB UMR5026, Université Bordeaux, F-33600 Pessac, France.

[4]Canadian Light Source, 44 Innovation Boulevard, Saskatoon, Sk, S7N 2V3, Canada

*corresponding author

goward@mcmaster.ca

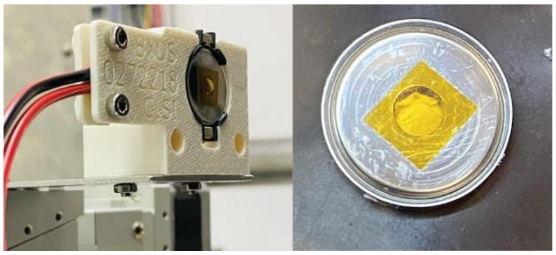

Figure S1. Photographs of (a) The custom-built cell holder and (b) a modified coin cell used for the *operando* studies.

^{7}Li MAS NMR Experimental description

The pristine samples were collected using the same parameters. ^{7}Li MAS NMR experiments were acquired using a Bruker Avance III HD spectrometer operating at a Larmor frequency of 116.64 MHz (7.05 T) using a Bruker 1.3 mm HX probe at a spinning frequency of 60 kHz. The spectra are referenced to 1M $LiCl_{(aq)}$ at 0 ppm. One-dimensional ^{7}Li MAS spectra were obtained using a double spin echo pulse sequence utilizing short, high-power adiabatic pulses (SHAPs)[1] following a 1.25 μs $\frac{\pi}{2}$ excitation pulse. The SHAPs utilized a tanh/tan shape, a 5 MHz frequency sweep, and were 50 microseconds in length with a maximum RF field strength of 200 kHz. Under these conditions, the SHAPs are expected to be >99% efficient.[2] T_1 relaxation times were determined using a standard inversion-recovery sequence.

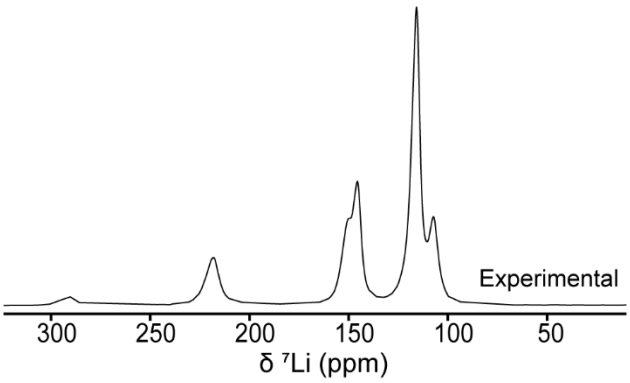

Figure S2. ^{7}Li MAS ssNMR spectrum of pristine $LiFeV_2O_7$.

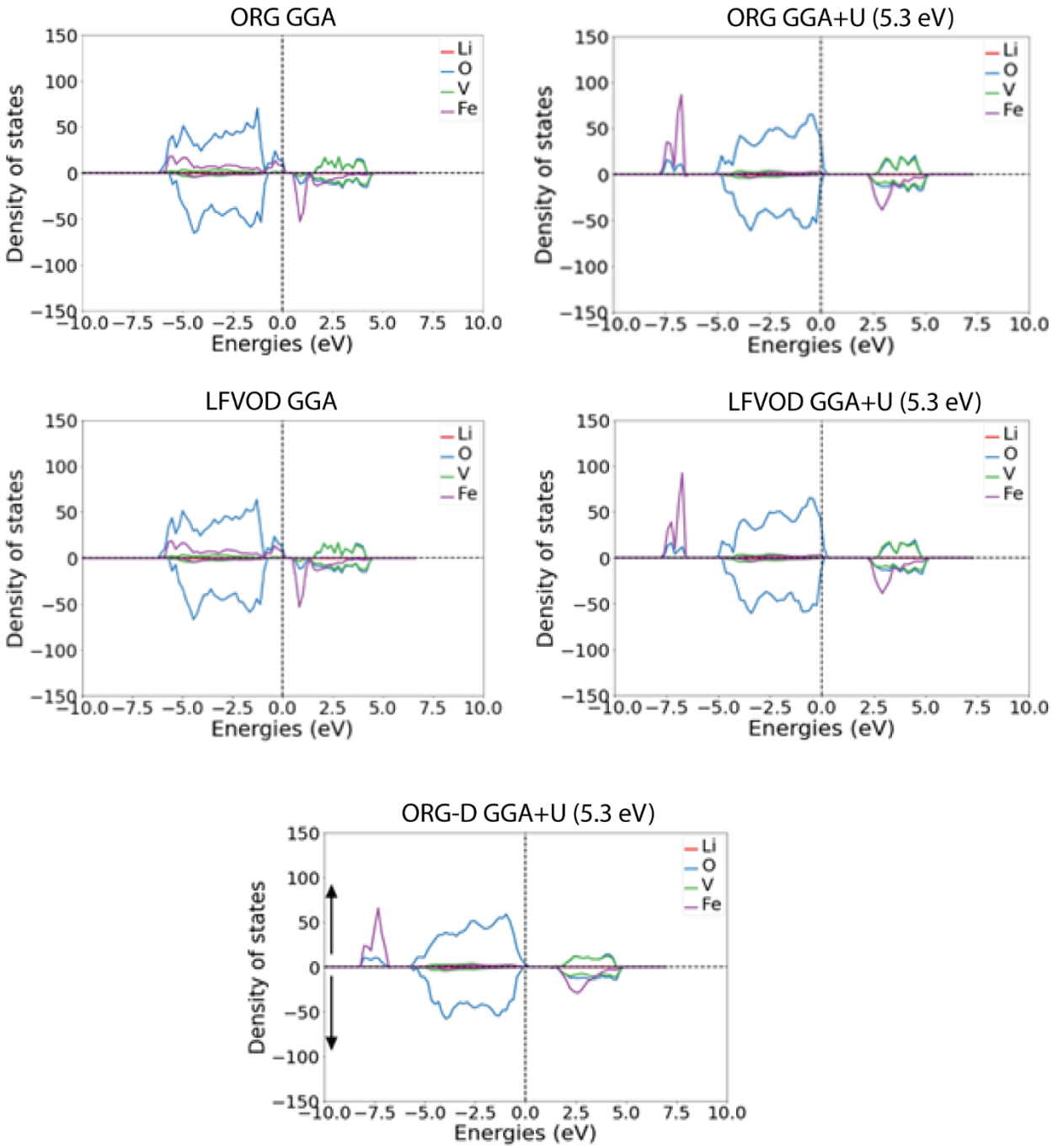

Figure S3. Calculated total spin DOS for the three models of $LiFeV_2O_7$ (ORG, LFVOD, and ORG-D) with GGA and GGAU where the color coding of lines are elements.

Table S1: Calculated Fermi contact shifts for Li sites in ORG and LFVOD structures calculated using GGA and GGA+U methods.

Atom	EXP		Calculated ^{7}Li shifts (ppm)					
			ORG GGA	ORG GGA+U (5.3 eV)	ORG GGA+U (4.3 eV)	ORG GGA+U (3.5 eV)	LFVOD GGA	LFVOD GGA+U (5.3 eV)
Li1	146	150.2	339.2	184.5	192.4	207.9	323.4	176.9
Li2	219		454.9	276.8	300.2	323.4	338.9	284.5
Li3	107.2	115.6	262.1	169.2	215.5	238.7	238.8	176.9
Extra Signal	292							

Table S2. Calculated Li-Fe distances and Li-O-Fe angle using GGA approach.

ORG			**LFVOD**		
Site	dLi-Fe (Å)	Li-O-Fe angles (°)	Site	dLi-Fe (Å)	Li-O-Fe angles (°)
Li1	Li1-Fe3 = 3.1199 Li1-Fe2 = 4.3147	Li1-O21-Fe2 = 139.51 Li1-O19-Fe3 = 100.72 Li1-O03-Fe3 = 92.41	Li1	Li1-Fe3 = 3.14778 Li1-Fe2 = 3.72287	Li1-O21-Fe2 = 129.25 Li1-O03-Fe3 = 93.80 Li1-O19-Fe3 = 101.88
Li2	Li2-Fe2 = 3.0527 Li2-Fe3 = 3.4602 Li2-Fe1 = 3.5226	Li2-O04-Fe2 = 98.55 Li2-O18-Fe2 = 96.47 Li2-O20-Fe1 = 118.49 Li2-O02-Fe3 = 112.51	Li2	Li2-Fe2 = 3.0559 Li2-Fe3 = 3.5075 Li2-Fe1 = 3.47579	Li2-O18-Fe2 = 96.88 Li2-O4-Fe2 = 98.85 Li2-O02-Fe1 = 113.83 Li2-O20-Fe3 = 117.45
Li3	Li3-Fe1 = 3.18089 Li3-Fe2 = 3.73974	Li3-O15-Fe1 = 102.79 Li3-O09-Fe1 = 94.33 Li3-O01-Fe2 = 129.53	Li3	Li3-Fe1 = 3.15090 Li3-Fe2 = 3.14713	Li3-O09-Fe1 = 99.03 Li3-O15-Fe1 = 100.24 Li3-O01-Fe2 = 140.21

Table S3. Calculated Li-Fe distances and Li-O-Fe angle using GGA+U (5.3 eV) approach.

ORG			**LFVOD**		
Site	dLi-Fe (Å)	Li-O-Fe angles (°)	Site	dLi-Fe (Å)	Li-O-Fe angles (°)
Li1	Li1-Fe3 = 3.1389 Li1-Fe2 = 4.3273	Li1-O21-Fe2 = 140.12 Li1-O19-Fe3 = 100.70 Li1-O03-Fe3 = 100.70	Li1	Li1-Fe3 = 3.1716 Li1-Fe2 = 3.7070	Li1-O21-Fe2 = 129.88 Li1-O03-Fe3 = 95.75 Li1-O19-Fe3 = 101.39
Li2	Li2-Fe2 = 3.0421 Li2-Fe3 = 3.4569 Li2-Fe1 = 3.5458	Li2-O04-Fe2 = 97.96 Li2-O18-Fe2 = 96.80 Li2-O20-Fe1 = 118.76 Li2-O02-Fe3 = 112.72	Li2	Li2-Fe2 = 3.0368 Li2-Fe3 = 3.5171 Li2-Fe1 = 3.4789	Li2-O18-Fe2 = 96.97 Li2-O04-Fe2 = 98.67 Li2-O02-Fe1 = 114.66 Li2-O20-Fe3 = 118.13
Li3	Li3-Fe1 = 3.1790 Li3-Fe2 = 3.7448	Li3-O15-Fe1 = 102.59 Li3-O09-Fe1 = 94.74 Li3-O01-Fe2 = 129.57	Li3	Li3-Fe1 = 3.1509 Li3-Fe2 = 4.2966	Li3-O09-Fe1 = 98.71 Li3-O15-Fe1 = 100.54 Li3-O01-Fe2 = 141.77

Table S4. Calculated Li-Fe distances and Li-O-Fe angle for ORG-D using GGA+U (5.3 eV) approach.

ORG site	ORG-D Site	dLi-Fe (Å)	Li-O-Fe angles (°)
Li1	$Li1_a$	$Li1_a$-Fe3 = 3.1722 $Li1_a$-Fe2 = 4.2526	$Li1_a$-O19-Fe3 = 102.71 $Li1_a$-O21-Fe2 = 138.94 $Li1_a$-O03-Fe3 = 97.30
Li1	$Li1_b$	$Li1_b$-Fe3 = 3.2005 $Li1_b$-Fe2 = 4.2014	$Li1_b$-O03-Fe3 = 99.96 $Li1_b$-O19-Fe3 = 100.51 $Li1_b$-O21-Fe2 = 140.56
Li1	$Li1_c$	$Li1_c$-Fe3 = 3.1379 $Li1_c$-Fe2 = 4.2804	$Li1_c$-O19-Fe3 = 100.68 $Li1_c$-O03-Fe3 = 98.64 $Li1_c$-O21-Fe2 = 141.72
Li1	$Li1_d$	$Li1_d$-Fe3 = 3.1527 $Li1_d$-Fe2 = 4.1537	$Li1_d$-O03-Fe3 = 97.25 $Li1_d$-O19-Fe3 = 101.91 $Li1_d$-O21-Fe2 = 138.20
Li2	$Li2_a$	$Li2_a$-Fe2 = 3.0020 $Li2_a$-Fe3 = 3.4707 $Li2_a$-Fe1 = 3.4946	$Li2_a$-O02-Fe3 = 114.11 $Li2_a$-O20-Fe1 = 117.48 $Li2_a$-O04-Fe2 = 98.04 $Li2_a$-O18-Fe2 = 96.55
Li2	$Li2_b$	$Li2_b$-Fe2 = 2.9785 $Li2_b$-Fe3 = 3.4663 $Li2_b$-Fe1 = 3.5999	$Li2_b$-O04-Fe2 = 98.04 $Li2_b$-O18-Fe2 = 96.20 $Li2_b$-O02-Fe3 = 112.90 $Li2_b$-O29-Fe1 = 118.13
Li2	$Li2_c$	$Li2_c$-Fe2 = 3.0699 $Li2_c$-Fe3 = 3.3429 $Li2_c$-Fe1 = 3.6970	$Li2_c$-O02-Fe3 = 111.69 $Li2_c$-O20-Fe1 = 117.57 $Li2_c$-O18-Fe2 = 97.07 $Li2_c$-O04-Fe2 = 102.29
Li2	$Li2_d$	$Li2_d$-Fe2 = 3.0631 $Li2_d$-Fe3 = 3.5162 $Li2_d$-Fe1= 3.5750	$Li2_d$-O18-Fe2 = 98.09 $Li2_d$-O04-Fe2 = 99.01 $Li2_d$-O02-Fe3 = 112.63 $Li2_d$-O20-Fe1 = 118.52
Li3	$Li3_a$	$Li3_a$-Fe1 = 3.1700 $Li3_a$-Fe2 = 3.8507	$Li3_a$-O01-Fe2 = 132.47 $Li3_a$-O15-Fe1 = 102.32 $Li3_a$-O09-Fe1 = 97.81
Li3	$Li3_b$	$Li3_b$-Fe1 = 3.1103 $Li3_b$-Fe2 = 3.8206	$Li3_b$-O09-Fe1 = 93.45 $Li3_b$-O15-Fe1 = 102.26 $Li3_b$-O01-Fe2 = 131.19
Li3	$Li3_c$	$Li3_c$-Fe1 = 3.1847 $Li3_c$-Fe2 = 4.005	$Li3_c$-O15-Fe1 = 101.93 $Li3_c$-O09-Fe1 = 98.75 $Li3_c$-O01-Fe2 = 137.60
Li3	$Li3_d$	$Li3_d$-Fe1 = 3.1649 $Li3_d$-Fe2 = 3.7304	$Li3_d$-O15-Fe1 = 101.28 $Li3_d$-O09-Fe1 = 96.69 $Li3_d$-O01-Fe2 = 129.27

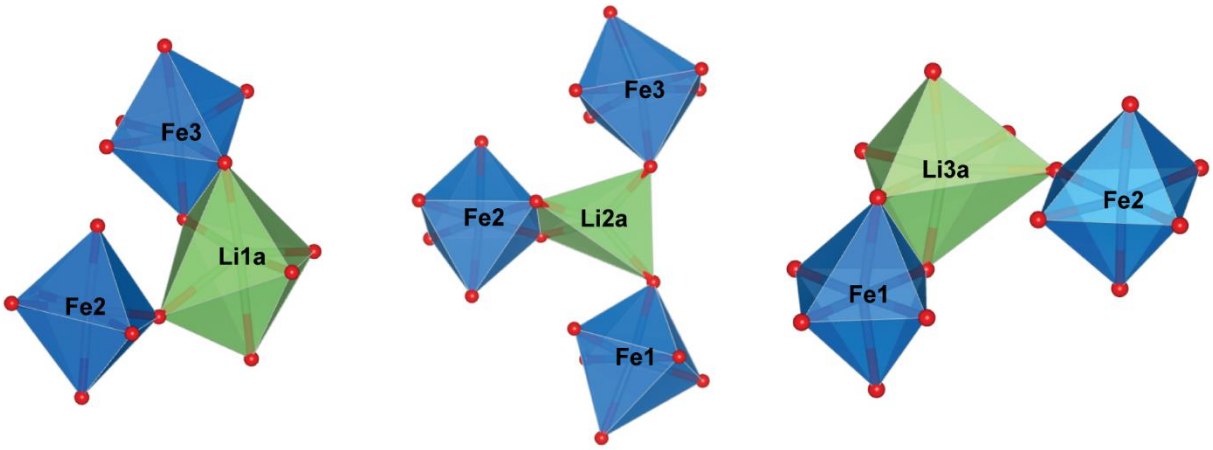

Figure S4. Environment for the three Li sites of ORG-D showing the local geometry. (a) $Li1_a$ (b) $Li2_a$ and (c) $Li3_a$.

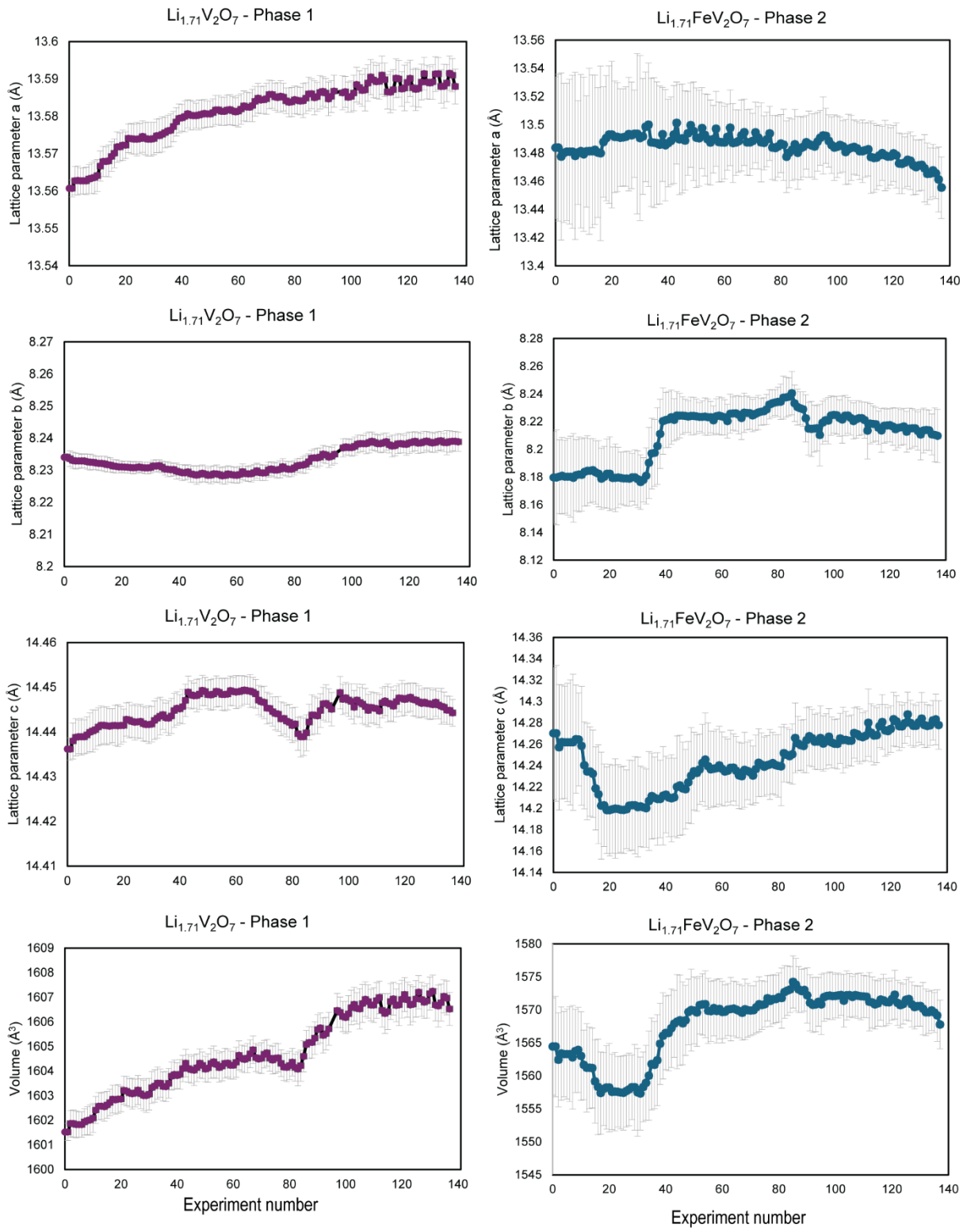

Figure S5. Lattice parameter and unit cell volume change during the first discharge cycle.

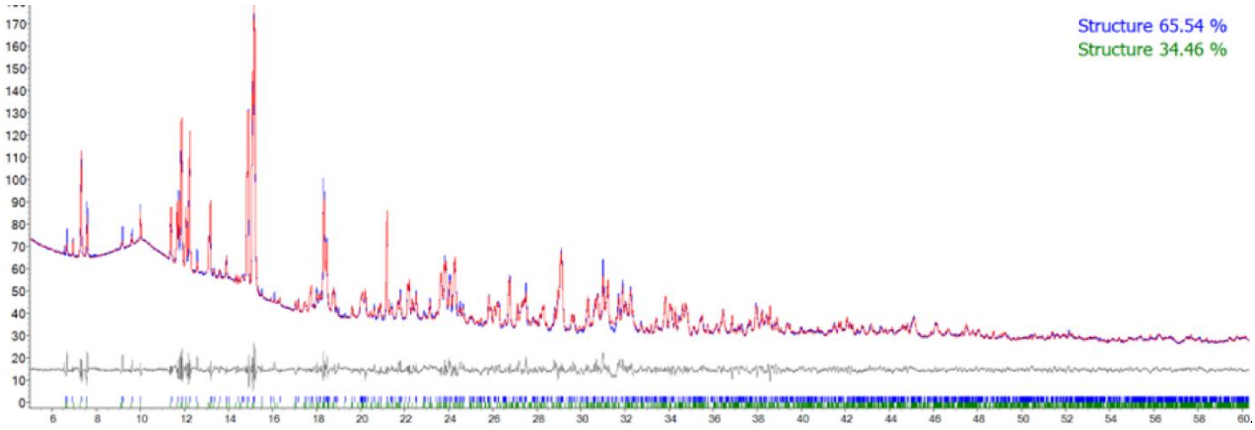

Figure S6. Rietveld refinement profile obtained for $Li_{1.71}V_2O_7$ from the synchrotron XRPD pattern.

Table S5. Relaxed cell parameters for GGA+U optimized $Li_{1.71}FeV_2O_7$ Phase 1 compared to values obtained from Rietveld refinement.

Unit cell parameters	$Li_{1.71}FeV_2O_7$* Phase 1	$Li_{1.71}FeV_2O_7$ Phase1 – GGAU
a (Å)	13.595(2)	13.875(5)
b (Å)	8.2503(3)	8.3760(2)
c (Å)	14.2166(1)	14.4034(5)
β (°)	94.866(5)	95.874(0)
Volume (Å)^3	1588.7(7)	1665.1(7)

* Data obtained from the Rietveld refinement of $Li_{1.71}FeV_2O_7$ for phase 1.

Table S6: Calculated shifts for Li sites by GGA+U method for the ORG-D structure.

$Li_{1.71}FeV_2O_7$ Phase 1		
CIF site	**Site**	**Fermi Shift ^{7}Li (ppm)**
Li1	$Li1_a$	59.5
Li1	$Li1_b$	394.5
Li1	$Li1_c$	-29.77
Li1	$Li1_d$	387.0
Li2	$Li2_a$	223.3
Li2	$Li2_b$	253.0
Li2	$Li2_c$	156.2
Li2	$Li2_d$	119.1
Li3	$Li3_a$	215.8
Li3	$Li3_b$	133.9
Li3	$Li3_c$	104.2
Li3	$Li3_d$	141.4
New	Li13	59.5
New	Li14	-104.2
New	Li15	66.98
New	Li16	-96.7
New	Li17	-141.4
New	Li18	74.4
New	Li19	-89.3
New	Li20	29.77

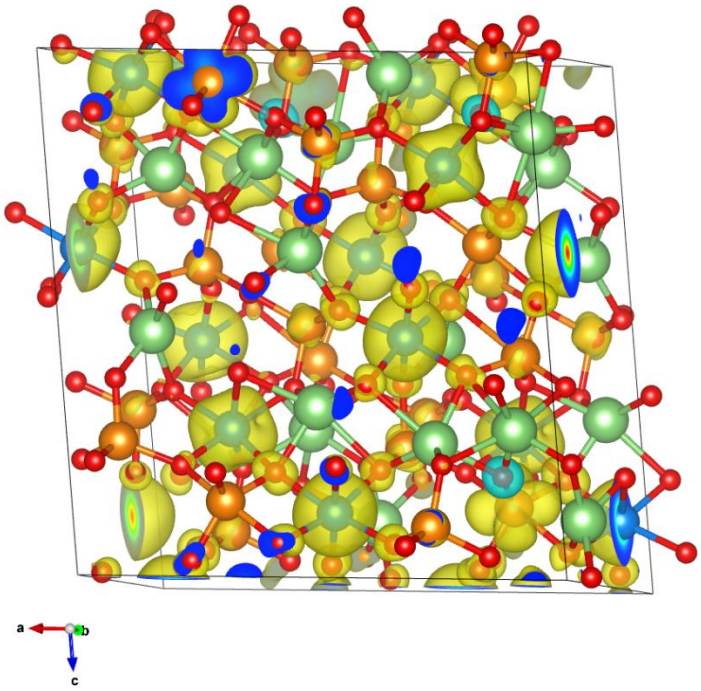

Figure S7. 3D spin density map calculated for $Li_{1.71}FeV_2O_7$ Phase1with GGA+U and isosurfaces value equal to 0.005 spin/Å^2. The positive and negative electron spin densities map are represented in yellow and blue, respectively.