Supplementary information

Figure S1: Difference Fourier map between synchrotron X-ray diffraction observation and calculation, considering the host structure [$FeBO_3$] only (Left y=0.5), [$LiBO_3$] only (Right y=0.3281). The positive electronic density residue was marked as red while the negative was painted in light blue.

Figure S2: Difference Fourier map between neutron powder diffraction observation (neutron diffraction) and calculation of considering the host structure [$FeBO_3$] only (Left y=0.5), [$LiBO_3$] only (Right y=0.3281). The positive nuclear residue was marked as red while the negative was painted in light blue.

Figure S3: Illustration of the zigzag shaped Li^+ diffusion path along the ***c-axis*** (adapted from the cif file of our single crystal XRD refinement). Light blue plane (010) and grey dash line (lithium ions diffusion path) are guided for eyes.

Figure S4: Comparison of XRD patterns: non-carbon coated $LiFeBO_3$ (sample **A**) versus carbon-coated $LiFeBO_3$/C (Sample **C**, ascorbic acid decomposition), recorded with a Bruker D8 diffractometer using CoK_α radiation. The cell parameters deduced from full-pattern matching refinements are listed on right side of the figure.

Figure S5: Full-pattern matching refinement conducted on XRD diffraction pattern recorded from $LiFeBO_3$/C sample prepared by self-combustion; (left inset) comparison of partial XRD patterns of self-combustion prepared $LiFBO_3$/C (green) and non-carbon coated $LiFeBO_3$ (red); (right inset) TEM image of sample B (self-combustion), suggested that $LiFeBO_3$ grains are surrounded by carbon.

Figure S6: (a) Charge and discharge curves for sample (C) cycled at C/20 rate, 55°C within 1.5-4.5 V voltage range, using LP30 liquid electrolyte. (b) Capacity retention for the same cell, which could still deliver a capacity of 350 mAh/g at the 70^{th} cycle.

Figure S7: *in-situ* XRD patterns recorded during battery operation (1st charge to 4.5 V and 1st discharge down to 1.5 V vs. Li^+/Li) with a Bruker D8 diffractometer using the CuK_α radiation. The cell was cycled at C/50 rate, meanwhile XRD patterns were collected every 2 hours for a 10°-40° 2θ range. The red and blue dash lines are guided for eyes.

Figure S8: Selected 2θ regions of XRD patterns showing the respective shifts of the reflection peaks; the pristine $LiFeBO_3$ (upper red curve), "$Li_{0.25}FeBO_3$" (green curves) and $LiFeBO_3$ after one full electrochemical cycle (lower red curve).

Table S1. Crystallographic data of $LiFeBO_3$ derived from Synchrotron X-Ray diffraction Rietveld refinements, global agreement factors and selected interatomic distances(Å) and angles(deg.)

Formula	Atom	S.O.F.	X	y	z	B_{iso}(Å^2)
$LiFeBO_3$	**Li(1)**	0.39(3)	0.698(4)	0.525(2)	0.164(2)	0.63(4)
C2/c	**Li(2)**	0.60(3)	0.632(3)	0.487(2)	0.1078(15)	1.73(7)
a = 5.1701(1)Å	**Fe**	1.0	0.1612(2)	0.3361(1)	0.1243(1)	anisotropic
b = 8.99219(2)Å	**B**	1.0	0.152(1)	0.6733(8)	0.1233(5)	0.71(3)
c = 10.1656(2)Å	**O1**	1.0	0.4058(5)	0.1625(4)	0.0922(3)	0.78(9)
β = 91.443(1)°	**O2**	1.0	0.7777(5)	0.3030(3)	0.1568(3)	0.55(5)
V = 468.76 (1) Å^3	**O3**	1.0	0.3129(6)	0.5428(3)	0.1264(3)	0.78(9)
		R_{Bragg}=6.70% R_f=4.98% R_p=10.4% R_{wp}=13.5 χ^2=1.24				

1Fe 2Li model -- anisotropic thermal parameters (Å^2)x10^{-4}

Atom	U11	U22	U33	U12	U13	U23
Fe	97(4)	60 (3)	156(4)	18(5)	11(3)	6(5)

The form of the anisotropic thermal parameters is:
$\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23}]$

BO_3

	O1	***O2***	***O3***
O1	**1.310(6)**	125.0(4)	120.4(4)
O2	2.374(3)	**1.364(7)**	114.5(5)
O3	2.377(4)	2.349(3)	**1.428(7)**

$Li(1)O_4$

	O1	***O2***	***O3***	***'Axial' O3***
O1	**1.797(19)**	121.9(9)	117.7(9)	112.6(9)
O2	3.343(4)	**2.024(18)**	105.6(8)	96.8(7)
O3	3.272(4)	3.226(3)	**2.024(20)**	97.5(8)
'Axial' O3	3.281(4)	3.115(4)	3.132(4)	**2.138(20)**

$Li(2)O_4$

	O1	***O2***	***O3***	***'Axial' O3***
O1	**2.119(17)**	113.7(8)	115.7(8)	84.96(5)
O2	3.343(4)	**1.868(17)**	126.8(9)	96.2(6)
O3	3.272(4)	3.226(3)	**1.738(16)**	105.9(7)
'Axial' O3	3.073(4)	3.214(4)	3.343(4)	**2.419(15)**

FeO_5

	O1	***O2***	***O3***	***Axial O1***	***Axial O2***
O1	**2.031(3)**	121.8(1)	117.2(1)	85.8(1)	89.2(1)
O2	3.557(3)	**2.039(2)**	120.8(1)	91.8(1)	86.2(1)
O3	3.445(4)	3.517(4)	**2.003(2)**	93.2(1)	93.7(1)
Axial O1	2.897(4)	3.064(4)	3.073(4)	**2.220(3)**	172.7(1)
Axial O2	3.017(4)	2.941(3)	3.115(4)	4.469(4)	**2.258(3)**

Table S2a Mössbauer parameters of $LiFeBO_3$ at 293K

	CS (mm/s)	**QS** (mm/s)	A (counts·mm/s)	**w+** (mm/s)	**Site**$_{population}$ **(%)**
$Fe^{2+}1$	0.919(32)	1.900(63)	3100	0.097(81)	3.2(7)
$Fe^{2+}2$	1.0648(43)	1.4006(91)	35700	0.1369(54)	37.7(2)
$Fe^{2+}3$	1.120(28)	1.977(12)	28000	0.148(17)	29.0(2)
$Fe^{2+}4$	1.012(33)	1.996(27)	18000	0.136(63)	19.0(2)
Fe^{3+}	0.188(49)	0.472(85)	7890	0.166(40)	8.35(64)
Fe	/	/	1900	/	2.01(87)

CS—chemical shifts, QS—quadrupole splitting, w+—line width

Table S2b *Mössbauer parameters of $LiFeBO_3$ at 70K*

	CS (mm/s)	**QS** (mm/s)	**A** (counts·mm/s)	**w+** (mm/s)	**Site**$_{population}$ **(%)**
$Fe^{2+}1$	1.377(12)	2.050(19)	8200	0.098(15)	3.76(68)
$Fe^{2+}2$	1.1735(35)	1.870(21)	60000	0.173(15)	27.8(5)
$Fe^{2+}3$	1.1838(12)	2.7007(43)	95600	0.1462(24)	44.0(2)
$Fe^{2+}4$	1.1856(27)	1.467(17)	34500	0.126(13)	15.9(4)
Fe^{3+}	0.2731(67)	0.637(14)	14910	0.1181(93)	6.86(30)
Fe	/	/	3700	/	1.72(54)

Table. S3 Crystallographic data of $LiFeBO_3$ from room temperature single crystal X-ray diffraction and Selected interatomic distances (Å) and angles (deg.).

Formula	Atom	S.O.F.	x	y	Z	B_{iso}(Å²)
$LiFeBO_3$	Li(1)	0.53(5)	0.664(1)	0.508(1)	0.157(2)	1.07
C*2/*c	Li(2)	0.47(5)	0.661(1)	0.495(1)	0.093(3)	1.18
a = 5.1711(5)Å	Fe	1.0	0.16114(5)	0.33586(3)	0.12456(3)	0.81
b = 8.9103(8)Å	B	1.0	0.1657(3)	0.6687(2)	0.1253(2)	0.56
c = 10.1577(10)Å	O1	1.0	0.4045(2)	0.1616(2)	0.0921(3)	0.70
β = 91.475(4)°	O2	1.0	0.7808(2)	0.3041(2)	0.1576(1)	0.66
V = 467.87(8) Å³	O3	1.0	0.3120(3)	0.5404(2)	0.1261(2)	1.51
			$R[F^2>2\sigma(F^2)]=0.023$ $wR(F^2)=0.072$			

1Fe 2Li model -- anisotropic thermal parameters (Å²)x10^{-4}

Atom	U11	U22	U33	U12	U13	U23
Fe	89(2)	99(2)	122(1)	-6(1)	2(1)	7(1)
O3	80(5)	50(5)	441(5)	-27(4)	-47(4)	8(4)

The form of the anisotropic thermal parameters is:
$\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23}]$

BO_3

	O1	*O2*	*O3*
O1	**1.385(2)**	120.6(2)	119.8(3)
O2	2.403(2)	**1.381(3)**	119.5(2)
O3	2.385(2)	2.377(2)	**1.371(3)**

$Li(1)O_4$

	O1	*O2*	*O3*	*'Axial' O3*
O1	**1.969(10)**	117.2(3)	117.5(5)	103.0(4)
O2	3.320(2)	**1.921(9)**	116.7(4)	96.2(4)
O3	3.275(2)	3.221(2)	**1.861(8)**	100.2(3)
'Axial' O3	3.283(3)	3.090(3)	3.141(3)	**2.22(3)**

$Li(2)O_4$

	O1	*O2*	*O3*	*'Axial' O3*
O1	**1.944(10)**	118.2(3)	117.6(6)	92.6(4)
O2	3.320(2)	**1.925(14)**	115.4(5)	100.5(5)
O3	3.275(2)	3.221(2)	**1.886(10)**	106.9(4)
'Axial' O3	3.045(3)	3.222(3)	3.334(3)	**2.26(4)**

FeO_5

	O1	*O2*	*O3*	*Axial O1*	*Axial O2*
O1	**2.031(1)**	121.9(1)	117.3(1)	85.8(1)	89.8(1)
O2	3.545(2)	**2.023(1)**	120.8(1)	92.4(1)	85.7(1)
O3	3.428(2)	3.483(2)	**1.982(2)**	92.8(1)	93.8(1)
Axial O1	2.895(2)	3.064(2)	3.045(3)	**2.218(1)**	173.3(1)
Axial O2	3.020(2)	2.906(2)	3.090(3)	4.454(2)	**2.243(1)**

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A