## Supporting Information

## Enhanced Performance Induced by Phase Transition of Li<sub>2</sub>FeSiO<sub>4</sub> upon Cycling at High Temperature

Titus Masese<sup>1,2,3\*</sup>, Yuki Orikasa<sup>4</sup>, Kentaro Yamamoto<sup>1</sup>, Yosuke Hori<sup>1</sup>, Rika Hagiwara<sup>5</sup> and Yoshiharu Uchimoto<sup>1\*</sup>

<sup>1</sup> Graduate School of Human and Environmental Studies, Kyoto University, Yoshidanihonmatsu-cho, Sakyo-ku, Kyoto, 606–8501, Japan.

<sup>2</sup> Research Institute of Electrochemical Energy (RIECEN), National Institute of Advanced Industrial Science and Technology (AIST), 1–8–31 Midorigaoka, Ikeda, Osaka 563–8577, Japan.

<sup>3</sup>AIST-Kyoto University Chemical Energy Materials Open Innovation Laboratory (ChEM-OIL), Sakyo-ku, Kyoto 606–8501, Japan.

<sup>4</sup> College of Life Sciences, Ritsumeikan University, 1–1–1 Noji-Higashi, Kusatsu, Shiga 525–8577, Japan.

<sup>5</sup> Graduate School of Energy Science, Kyoto University, Yoshida-nihonmatsu-cho, Sakyo–ku, Kyoto, 606–8501, Japan.

\*Correspondence to Titus Masese, Yoshiharu Uchimoto E-mail address: titus.masese@aist.go.jp, uchimoto.yoshiharu.2n@kyoto-u.ac.jp Phone: +81-72-751-8460 Fax: +81-72-751-9609



**Figure S1.** Rietveld refinement of synchrotron X–ray diffraction (XRD) data ( $5^{\circ} < 2\theta < 40^{\circ}$  range) for as-prepared Li<sub>2</sub>FeSiO<sub>4</sub>. The wavelength used was maintained at 0.50020(1) Å. Note that minor peaks arising from Fe impurity are excluded from the refinement.

**Table S1.** Atomic coordinates, site occupancies (g), and atomic displacement parameters  $(U_{iso})$  obtained from Rietveld refinement of synchrotron XRD data for as-prepared Li<sub>2</sub>FeSiO<sub>4</sub>, indexed in the monoclinic space group ( $P2_1/n$ ) with lattice constants a = 8.2433(4) Å, b = 5.0226(1) Å, c = 8.2373(3) Å, and  $\beta = 99.09$  (1) °. Atomic coordinates of Li were fixed according to those previously reported [1]. Atomic coordinates of Li and isotropic thermal factors of atoms were fixed according to those reported [1, *ibid*].

Atom	g	x	У	Z	$U_{ m iso}$
Lil	1.0	0.663	0.785	0.669	0.0093
Li2	1.0	0.585	0.193	0.084	0.0095
Fe1	0.9752(18)	0.2930(6)	0.7969(5)	0.5400(9)	0.0122
Sil	1.0	0.0436(12)	0.8102(10)	0.7905(7)	0.0062
O1	1.0	0.8548(21)	0.6905(9)	0.8256(19)	0.0065
O2	1.0	0.4261(14)	0.2132(13)	0.8852(12)	0.0065
O3	1.0	0.6958(19)	0.7685(26)	0.4343(31)	0.0065
O4	1.0	0.9584(16)	0.8568(8)	0.2172(17)	0.0065
$R_{\rm wp} = 3.69\%$	$R_{\rm p} = 2.57\%$	S (GOF) =	1.77		

2



**Figure S2.** Voltage (dis)charge profiles of  $Li_2FeSiO_4$  upon cycling at various current densities at 25 °C. Regardless of the rate used, a large voltage polarization was apparent at initial cycling process of  $Li_2FeSiO_4$  at room temperature. Note that the cut-off voltage was set at 1.3 V – 4.5 V.



**Figure S3.** Nyquist plots of Li<sub>2</sub>FeSiO<sub>4</sub> composite electrodes in the frequency range of 10 mHz and 100 kHz measured in (a) organic electrolyte (1M LiPF<sub>6</sub> in EC:EMC) within temperatures ranging from 15 °C to 55 °C and (b) ionic liquid (LiTFSA–CsTFSA (20:80) molten salt) within temperatures ranging from 140 °C to 170 °C. Inset in (a) shows the equivalent circuit. The Nyquist plots comprise a depressed semicircle at the high-frequency region and a straight line at the low-frequency region. In principle, the intercept at the Z' axis in the high-frequency regime represents the ohmic resistance ( $R_e$ ), corresponding to the resistance of the electrolyte. The semicircle in the low frequency range is related to the charge transfer resistance ( $R_{cl}$ ). Moreover, the straight line in the low-frequency regime is associated with lithium-ion (Li<sup>+</sup>) diffusion in Li<sub>2</sub>FeSiO<sub>4</sub>.



**Figure S4.** Arrhenius plots for (a) LiPF<sub>6</sub> organic electrolyte within temperature ranges of 15 °C–55 °C and (b) LiTFSA–CsTFSA (20:80) molten salt within temperature ranges of 140 °C –170 °C. These graphs show the ohmic resistance ( $R_e$ ) corresponding to the resistance of the electrolyte used. Details regarding the measurement protocols are described in the **Experimental** section.



**Figure S5.** Arrhenius plots for Li<sub>2</sub>FeSiO<sub>4</sub> indicating the charge transfer resistance ( $R_{ct}$ ) in (a) LiPF<sub>6</sub> organic electrolyte within temperature ranges of 15 °C–55 °C and (b) LiTFSA–CsTFSA (20:80) molten salt within temperature ranges of 140 °C–170 °C.



**Figure S6.** Linear relationship between the real impedance component ( $Z_{Re}$ ) and inverse square root of the low frequency region ( $\omega^{-1/2}$ ) for Li<sub>2</sub>FeSiO<sub>4</sub> in (a) LiPF<sub>6</sub> organic electrolyte within temperature ranges of 15 °C–55 °C and (b) LiTFSA–CsTFSA (20:80) molten salt within temperature ranges of 140 °C–170 °C.



**Figure S7.** Rietveld refinement of synchrotron XRD data ( $6.5^{\circ} < 2\theta < 40^{\circ}$  range) for delithiated LiFeSiO<sub>4</sub> obtained *ex situ* upon charging at 1C rate at 160°C. The wavelength was set at 0.50020(1) Å. Broad peaks that could not be properly indexed to the orthorhombic cell symmetry as well as Fe impurity peaks are excluded from the refinement.

**Table S2.** Atomic coordinates, site occupancies (g), and atomic displacement parameters  $(U_{iso})$  obtained from Rietveld refinement of synchrotron XRD data for delithiated LiFeSiO<sub>4</sub> (charged at 1C rate) in space group *Pnma* (orthorhombic) with lattice constants a = 10.2798(7) Å, b = 6.6011(5) Å, c = 5.0057(3) Å, and V = 339.6(1) Å<sup>3</sup>. Atomic coordinates were refined based on the crystallographic data previously reported [2]. Isotropic thermal factors of atoms were fixed according to those reported [2, *ibid*].

Atom	g	x	У	Z	$U_{ m iso}$
Li/Fe	0.6150/0.3850(20)	0.6576(6)	0.4990(6)	0.1830(10)	0.0126
Si	1.0	0.4146(4)	0.25	0.2875(9)	0.0079
O1	1.0	0.3937(9)	0.25	0.6254(15)	0.0059
O2	1.0	0.5559(8)	0.25	0.1977(15)	0.0038
O3	1.0	0.3428(9)	0.0728(6)	0.2090(16)	0.0215
$R_{\rm wp} = 2.52\%$	$R_{\rm p} = 1.92\%$	S (GOF) =	2.25		



**Figure S8.** Rietveld refinement of synchrotron XRD data ( $6.5^{\circ} < 2\theta < 40^{\circ}$  range) for delithiated LiFeSiO<sub>4</sub> obtained *ex situ* upon charging at C/10 rate at 160 °C. The wavelength was set at 0.50020(1) Å. Peaks that could not be properly indexed to the orthorhombic cell symmetry as well as Fe impurity peaks are excluded from the refinement.

**Table S3.** Atomic coordinates, site occupancies (g), and atomic displacement parameters  $(U_{iso})$  obtained from Rietveld refinement of synchrotron XRD data for delithiated LiFeSiO<sub>4</sub> (charged at C/10 rate) in space group *Pnma* (orthorhombic) with lattice constants a = 10.2712(4) Å, b = 6.5997(3) Å, c = 5.0033(1) Å, and V = 339.1(1) Å<sup>3</sup>. Atomic coordinates were refined based on the crystallographic data previously reported [2]. Isotropic thermal factors of atoms were fixed according to those reported [2, *ibid*].

Atom	g	x	У	Z	$U_{ m iso}$
Li/Fe	0.6025/0.3975(26)	0.6561(5)	0.4921(5)	0.1801(8)	0.0126
Si	1.0	0.4144(4)	0.25	0.2904(8)	0.0079
O1	1.0	0.3957(8)	0.25	0.6354(13)	0.0059
O2	1.0	0.5525(8)	0.25	0.2001(13)	0.0038
O3	1.0	0.3438(8)	0.0716(6)	0.2081(14)	0.0215
	<b>D</b>		1.0.4		

 $R_{\rm wp} = 2.40\%$   $R_{\rm p} = 1.85\%$  S (GOF) = 1.94



**Figure S9.** Rietveld refinement of synchrotron XRD data ( $6.5^{\circ} < 2\theta < 40^{\circ}$  range) for delithiated LiFeSiO<sub>4</sub> obtained *ex situ* upon charging at C/50 rate at 160 °C. The wavelength was set at 0.50020(1) Å. Peaks that could not be properly indexed to the orthorhombic cell symmetry as well as Fe impurity peaks are excluded from the refinement.

**Table S4.** Atomic coordinates, site occupancies, and atomic displacement parameters obtained from Rietveld refinement of synchrotron XRD data for delithiated LiFeSiO<sub>4</sub> (charged at C/50 rate) in space group *Pnma* (orthorhombic) with lattice constants a = 10.2642(6) Å, b = 6.5987 (4) Å, c = 5.0013 (3) Å, and V = 338.7 (1) Å<sup>3</sup>. Atomic coordinates were refined based on the crystallographic data previously reported [2]. Isotropic thermal factors of atoms were fixed according to those reported [2, *ibid*].

	Atom	g	x	У	Z	$U_{ m iso}$
]	Li/Fe	0.5999/0.4001(25)	0.6571(5)	0.4949(5)	0.1802(8)	0.0126
	Si	1.0	0.4154(4)	0.25	0.2902(8)	0.0079
	01	1.0	0.3953(8)	0.25	0.6274(13)	0.0059
	O2	1.0	0.5573(7)	0.25	0.2014(13)	0.0038
	O3	1.0	0.3438(8)	0.0690(6)	0.2129(13)	0.0215

 $R_{\rm wp} = 2.28\%$   $R_{\rm p} = 1.74\%$  S (GOF) = 1.76



**Figure S10.** Rietveld refinement of synchrotron XRD data ( $6.5^{\circ} < 2\theta < 40^{\circ}$  range) for relithiated Li<sub>2</sub>FeSiO<sub>4</sub> obtained *ex situ* upon discharging at 1 C rate at 160 °C. The wavelength was set at 0.50020(1) Å. Peaks that could not be properly indexed to the orthorhombic cell symmetry as well as Fe impurity peaks are excluded from the refinement.

**Table S5.** Atomic coordinates, site occupancies, and atomic displacement parameters obtained from Rietveld refinement of synchrotron XRD data for relithiated Li<sub>2</sub>FeSiO<sub>4</sub> (discharged at 1C rate) in space group  $Pmn2_1$  (orthorhombic) with lattice constants a = 6.2198(8) Å, b = 5.4340(6) Å, c = 5.0333(5) Å, and V = 170.2(1) Å<sup>3</sup>. Atomic coordinates were refined based on the crystallographic data previously reported by Armstrong *et al.* [1]. Atomic coordinates of Li and isotropic thermal factors of atoms were fixed according to those reported [1, *ibid*].

Atom	g	X	У	Z	$U_{ m iso}$
Lil	1.0	0	0.147	0.045	0.0089
Li2/Fe	0.5707/0.4293(41)	0.2484(8)	0.3216(11)	0.4005(4)	0.0051
Si	1.0	0.5	0.1680(19)	0.0249(12)	0.0051
O1	1.0	0.3024(15)	0.3317(24)	0.9002(36)	0.0215
O2	1.0	0	0.1214(25)	0.5268(24)	0.0012
O3	1.0	0.5	0.1793(71)	0.3760(36)	0.0013
$R_{\rm wn} = 3.41\%$	$R_{\rm n} = 2.49\%$	S(GOF) =	2 80		



**Figure S11.** Rietveld refinement of synchrotron XRD data ( $6.5^{\circ} < 2\theta < 40^{\circ}$  range) for relithiated Li<sub>2</sub>FeSiO<sub>4</sub> obtained *ex situ* upon discharging at C/10 rate at 160 °C. The wavelength was set at 0.50020(1) Å. Peaks that could not be properly indexed to the orthorhombic cell symmetry as well as Fe impurity peaks are excluded from the refinement.

**Table S6.** Atomic coordinates, site occupancies (g), and atomic displacement parameters  $(U_{iso})$  obtained from Rietveld refinement of synchrotron XRD data for relithiated Li<sub>2</sub>FeSiO<sub>4</sub> (discharged at C/10 rate) in space group  $Pmn2_1$  (orthorhombic) with lattice constants a = 6.2086(3) Å, b = 5.4319(3) Å, c = 5.0291(2) Å, and V = 169.6(0) Å<sup>3</sup>. Atomic coordinates were refined based on the crystallographic data previously reported by Armstrong *et al.* [1]. Atomic coordinates of Li and isotropic thermal factors of atoms were fixed according to those reported [1, *ibid*].

Atom	g	X	У	Z	$U_{ m iso}$
Li1	1.00	0	0.147	0.045	0.0089
Li2/Fe	0.6541/0.3459(83)	0.2518(7)	0.3360(13)	0.4148(4)	0.0056
Si	1.0	0.5	0.1690(12)	0.0024(11)	0.0051
O1	1.0	0.2729(13)	0.3302(19)	0.9010(14)	0.0215
O2	1.0	0	0.1143(19)	0.4222(19)	0.0012
O3	1.0	0.5	0.1678(26)	0.3354(24)	0.0012
$R_{\rm wp} = 3.29\%$	$R_{\rm n} = 2.39\%$	S(GOF) =	2 90		



**Figure S12.** Rietveld refinement of synchrotron XRD data ( $6.5^{\circ} < 2\theta < 40^{\circ}$  range) for relithiated Li<sub>2</sub>FeSiO<sub>4</sub> obtained *ex situ* upon discharging at C/50 rate at 160 °C. The wavelength was set at 0.50020(1) Å. Peaks that could not be properly indexed to the orthorhombic cell symmetry as well as Fe impurity peaks are excluded from the refinement.

**Table S7.** Atomic coordinates, site occupancies (g), and atomic displacement parameters  $(U_{iso})$  obtained from Rietveld refinement of synchrotron XRD data for relithiated Li<sub>2</sub>FeSiO<sub>4</sub> (discharged at C/50 rate) in space group *Pmn2*<sub>1</sub> (orthorhombic) with lattice constants a = 6.2496(16) Å, b = 5.3935(17) Å, c = 5.0330(8) Å, and V = 169.6(1) Å<sup>3</sup>. Atomic coordinates were refined based on the crystallographic data previously reported by Armstrong *et al.* [1]. Atomic coordinates of Li and isotropic thermal factors of atoms were fixed according to those reported [1, *ibid*].

Atom	g	x	У	Z	$U_{ m iso}$
Lil	1.0	0	0.147	0.045	0.0089
Li2/Fe	0.5546/0.4454(64)	0.2517(9)	0.3339(17)	0.4193(2)	0.0051
Si	1.0	0.5	0.1250(17)	0.0059(19)	0.0051
O1	1.0	0.2854(14)	0.3465(33)	0.9533(16)	0.0215
O2	1.0	0	0.1283(43)	0.3198(20)	0.0012
O3	1.0	0.5	0.1854(36)	0.3633(21)	0.0012
$R_{\rm wp} = 2.34\%$	$R_{\rm p} = 1.78\%$	S (GOF) =	1.72		

## References

(1) Armstrong, A. R.; Kuganathan, N.; Islam, M. S.; Bruce, P. G. J. Am. Chem. Soc. 2011, 133, 13031-13035.

(2) Masese, T.; Orikasa, Y.; Tassel, C.; Kim, J.; Minato, T.; Arai, H.; Mori, T.; Yamamoto, K.; Kobayashi, Y.; Kageyama, H.; Ogumi, Z.; Uchimoto, Y. *Chem. Mater.* **2014**, *26*, 1380-1384.