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

Supporting Information

Influence of relative humidity on structure and electrochemical performance of sustainable $LiFeSO_4F$ electrodes for Li-ion batteries

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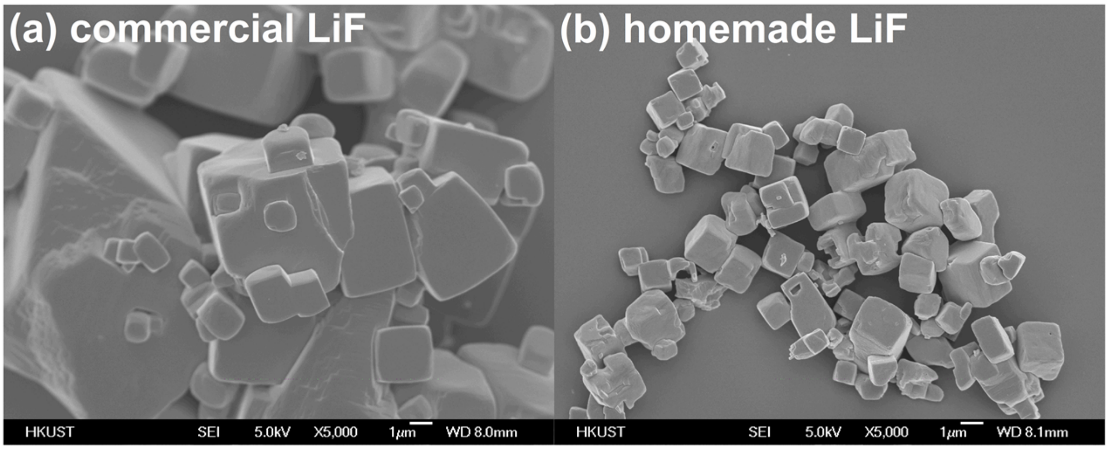

Fig. S1 SEM images of **(a)** commercial LiF and **(b)** homemade LiF. The dimension of LiF is significantly reduced by a precipitation reaction.

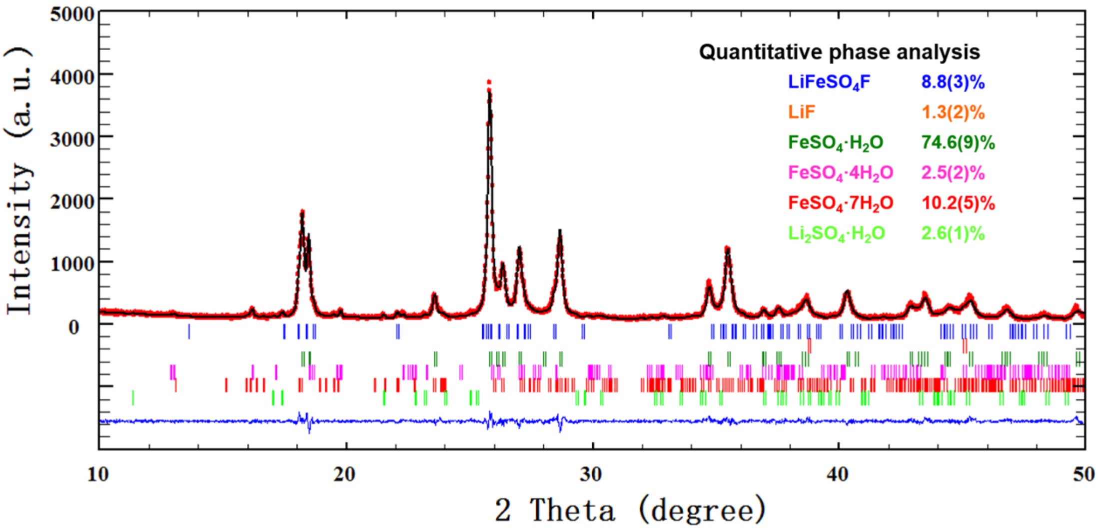

Fig. S2 Example of quantitative phase analysis for a tavorite-type LiFeSO$_4$F sample treated under 85% RH for 8 hours, determined from Rietveld refinement. The red dots and black lines are the observed and calculated intensities, respectively. The bottom blue line corresponds to the difference (obs-calc). Vertical tick marks are Bragg positions for each phase present in the sample, and the weight percentage of each phase is written with the same color code as the tick marks.

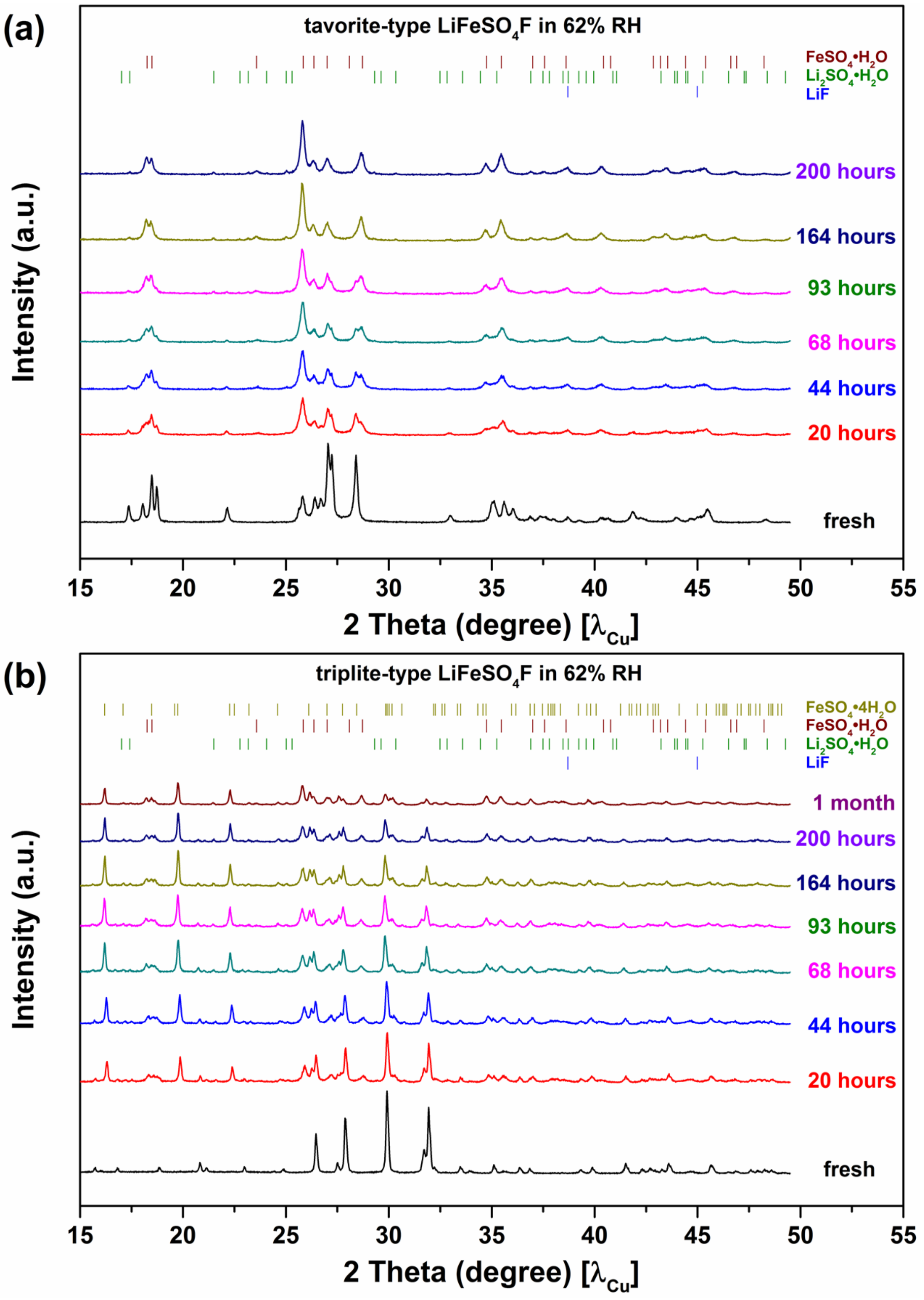

Fig. S3 Moisture influence on both **(a)** tavorite and **(b)** triplite LiFeSO$_4$F polymorphs at room temperature RH (62% at 25 ˚C). Tavorite-type LiFeSO$_4$F fully disappears after ~200 hours, while trace amount of triplite-type LiFeSO$_4$F can still be found after 1 month in 62% RH.

Water content measurement

Monitoring the moisture/water content of the material is essential to the understanding of sulfate decomposition. Unfortunately, the TGA analysis cannot precisely track the change in water content of the material before and after cycling, as water released from the bulk will react with $LiPF_6$ to form HF and other species. Instead, we checked this issue by examining (a) the structural change of moisture-affected material, and (b) the water content of the electrolyte.

(a) We checked the XRD spectra of $FeSO_4 \cdot 7H_2O$, the ultimate hydration product, before and after placing in the electrolyte. Commercial $FeSO_4 \cdot 7H_2O$ powders were placed in conventional electrolyte (1 M of $LiPF_6$ in EC/DMC) for one week, then recovered and dried under argon overnight. As shown in **Fig. S4 (a)**, the resulting powder was identified as the $FeSO_4 \cdot H_2O$ phase, implying that six water molecules are released to the electrolyte.

(b) Karl Fischer titration was performed on a series of controlled experiments to track the released water molecules in the electrolyte. $FeSO_4 \cdot 7H_2O$ powders were added to i. EC/DMC, ii. $LiClO_4$-EC/DMC, and iii $LiPF_6$-EC/DMC, and the corresponding water contents were analyzed. The initial water content was measured all below 20 ppm.

Fig. S4 (b) reveals that compared with pure EC/DMC, the presence of $LiClO_4$ favors the water release (8889.4 ppm > 4867.7 ppm). On the other hand, the relatively low water content of $LiPF_6$-based electrolyte strongly suggests that unlike $LiClO_4$, water molecules are consumed by $LiPF_6$ to form HF and other species.

With these evidences, we are able to conclude that water molecules depart from the moisture-affected sulfate material and diffuse to the electrolyte. In the $LiPF_6$-based system, excess amount of water will also react with $LiPF_6$.

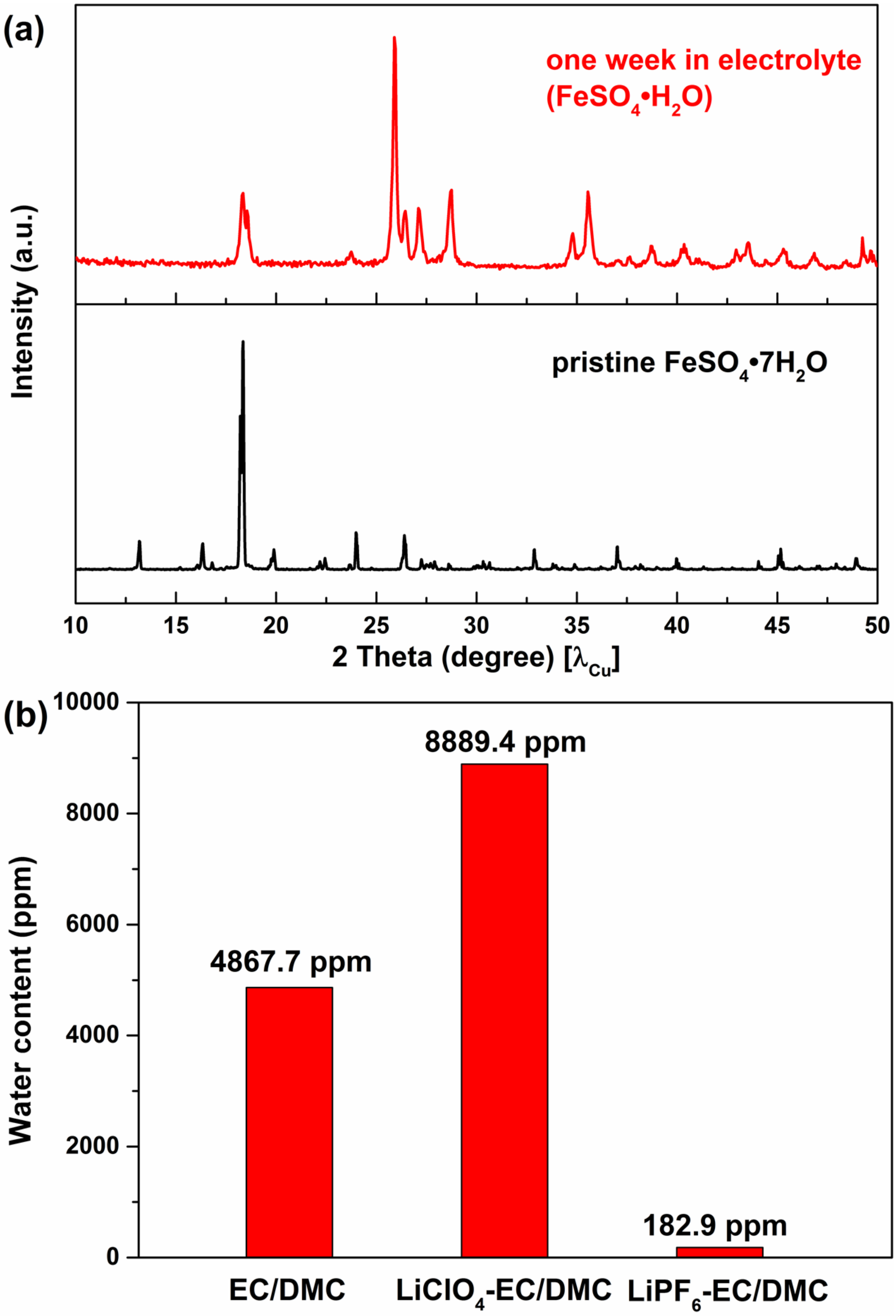

Fig. S4 **(a)** Structural change of $FeSO_4 \cdot 7H_2O$ in the electrolyte, and **(b)** impact of moisture-affected material on the water content of electrolytes

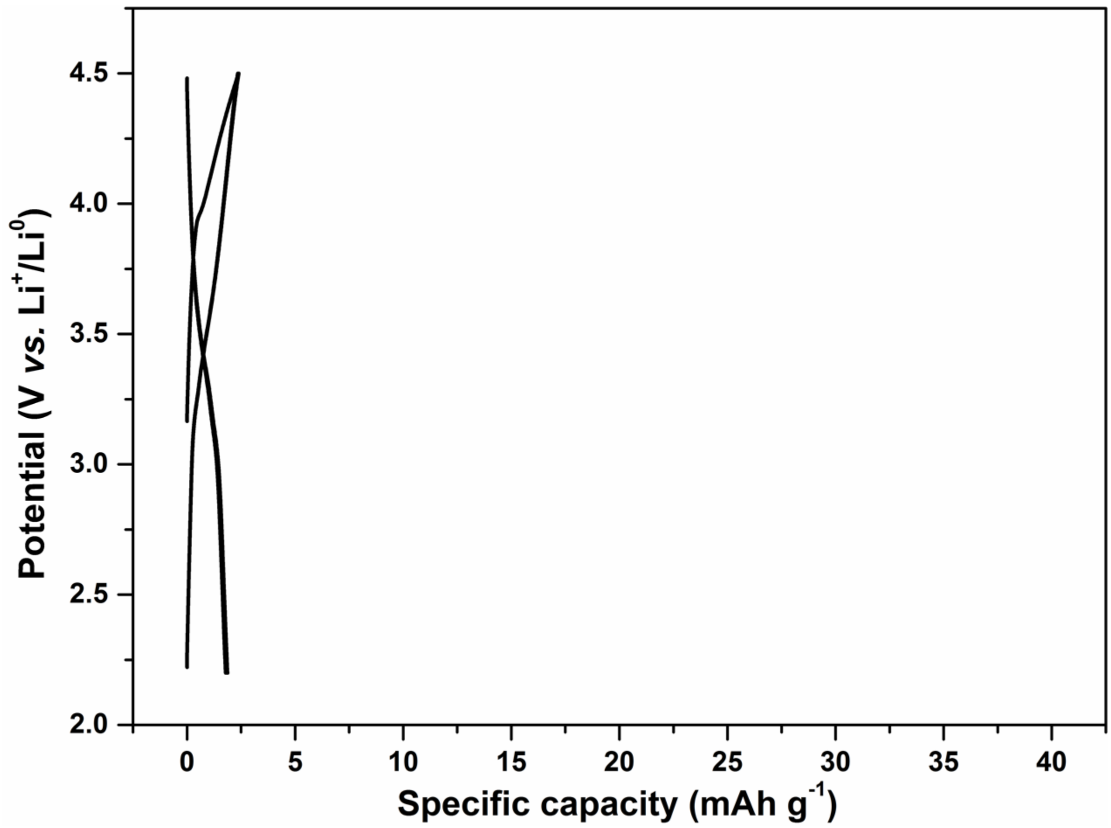

Fig. S5 First five cycles of the moisture-free $FeSO_4 \cdot H_2O$ sample, prepared by ball-milling $FeSO_4 \cdot H_2O$ with 20 wt% of carbon Super P in Ar and tested in a Swagelok-type cell. The cell was cycled in galvanostatic mode between 4.5 and 2.2 V *vs.* Li at a current density of C/20 (assuming $FeSO_4 \cdot H_2O$ could form $FeSO_4OH$ by the end of first charge, and reversibly exchange 1 Li^+ thereafter). No practical capacity was observed.

Experimental conditions and refined parameters of Mössbauer spectroscopy

Experimental conditions:
^{57}Fe Mössbauer spectra were measured on the raw materials to accurately characterize the oxidation state of iron in the obtained compounds. Absorbers were made by mixing 20 mg of the compounds with 60 mg of boron nitride. All the spectra have been recorded at room temperature in transmission geometry using a 0.25 Gbq source of ^{57}Co in Rh rhodium metal. The spectrometer was operated in transmission mode with a triangular velocity waveform, and a NaI scintillation detector was used for the detection of the gamma rays. The spectra, recorded between ±4 mm s^{-1}, were fitted with appropriate combination of Lorentzian lines using the PC-Mos II [G. Grosse, Technische Universität München Munich (Germany), 1993] computer program. In this way spectral parameters such as the isomer shift (IS), the electric quadrupole splitting (QS), the full linewidth at half maximum (LW) and the relative resonance areas (A) of the different components of the absorption patterns were determined.

Table S1. Refined Mössbauer parameters of **(a)** fresh $LiFeSO_4F$-C, **(b)** aged $LiFeSO_4F$-C in 85% RH for 2 hours, **(c)** discharge product of the wet-$LiFeSO_4F$-C after 40 cycles, and **(d)** reference $LiFeSO_4OH$-C at discharge state. Data in bold are compared with each other.

Sample	Comp.	IS (mm/s)	QS (mm/s)	LW (mm/s)	Area %	Attribution
Fresh $LiFeSO_4F$-C	1	1.32	2.81	0.32	36	Octa. Fe^{2+}
	2	1.31	2.21	0.54	64	Octa. Fe^{2+}
Aged $LiFeSO_4F$-C	2	1.27	2.70	0.49	80	$FeSO_4{\cdot}H_2O$
	3	0.45	0.54	0.41	20	Imp. Fe^{3+}
Discharged wet-$LiFeSO_4F$-C	1	1.27	2.64	0.38	47	$FeSO_4{\cdot}H_2O$
	2	**1.23**	**2.02**	**0.33**	33	**New Fe^{2+}**
	3	0.32	0.80	0.70	20	Imp. Fe^{3+}
Ref.[1]	1	**1.17**	**2.0**	**0.35**	86	**$LiFeSO_4OH$**
	2	1.23	2.5	0.32	8	$Li_{0.5}FeSO_4OH$
	3	0.41	1.58	0.32	6	$FeSO_4OH$

1 M. Ati, M. T. Sougrati, G. Rousse, N. Recham, M. L. Doublet, J. C. Jumas and J. M. Tarascon, *Chem. Mater.*, 2012, **24**, 1472–1485.