

Supporting Information

Oversaturated Li - FeOF Solid Solution Caused by LiPON Interfacial Coating

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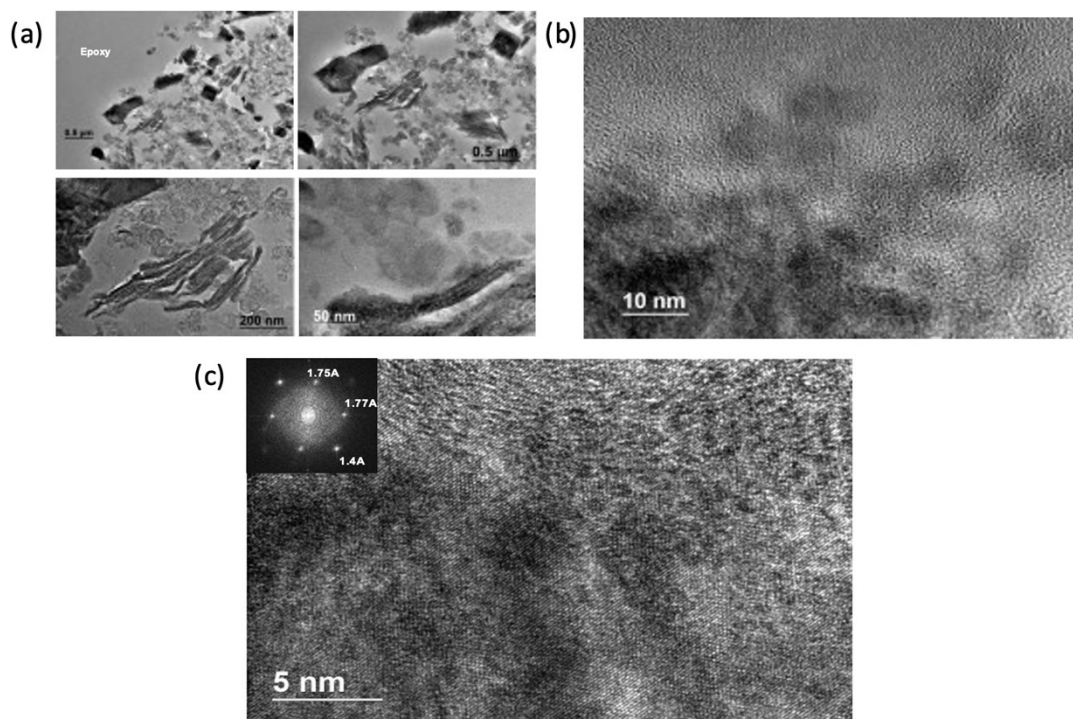


Figure S1. (a) TEM images of LiPON-coated-FeOF; (b-c) High-resolution image of LiPON-coated-FeOF, (c) Lattice image for FeOF along [01-1] zone axis.

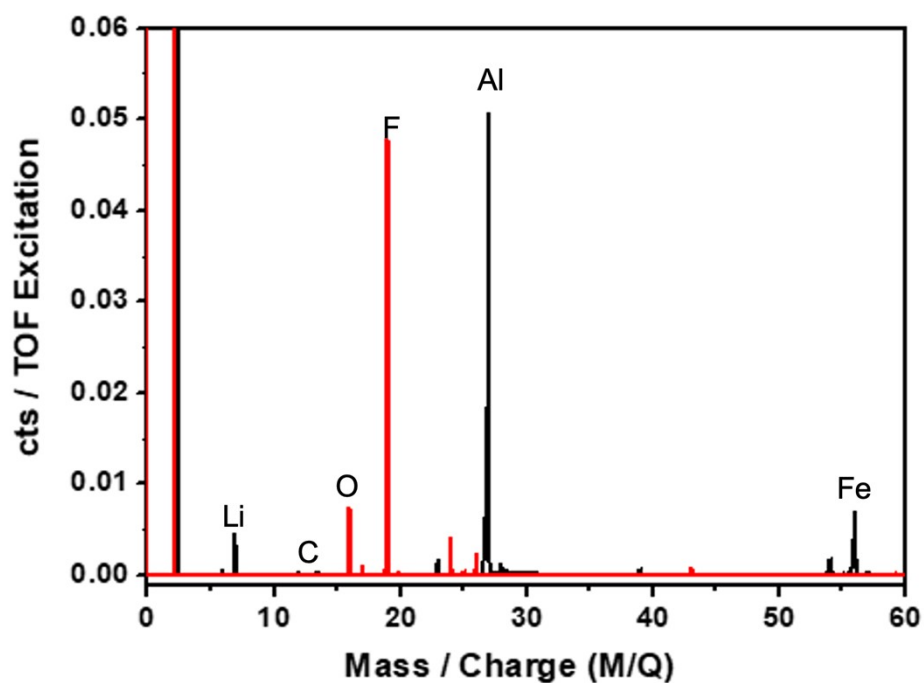


Figure S2. Time-of-Flight Second Ion Mass Spectra (ToF-SIMS) result of the LiPON coating on FeOF.

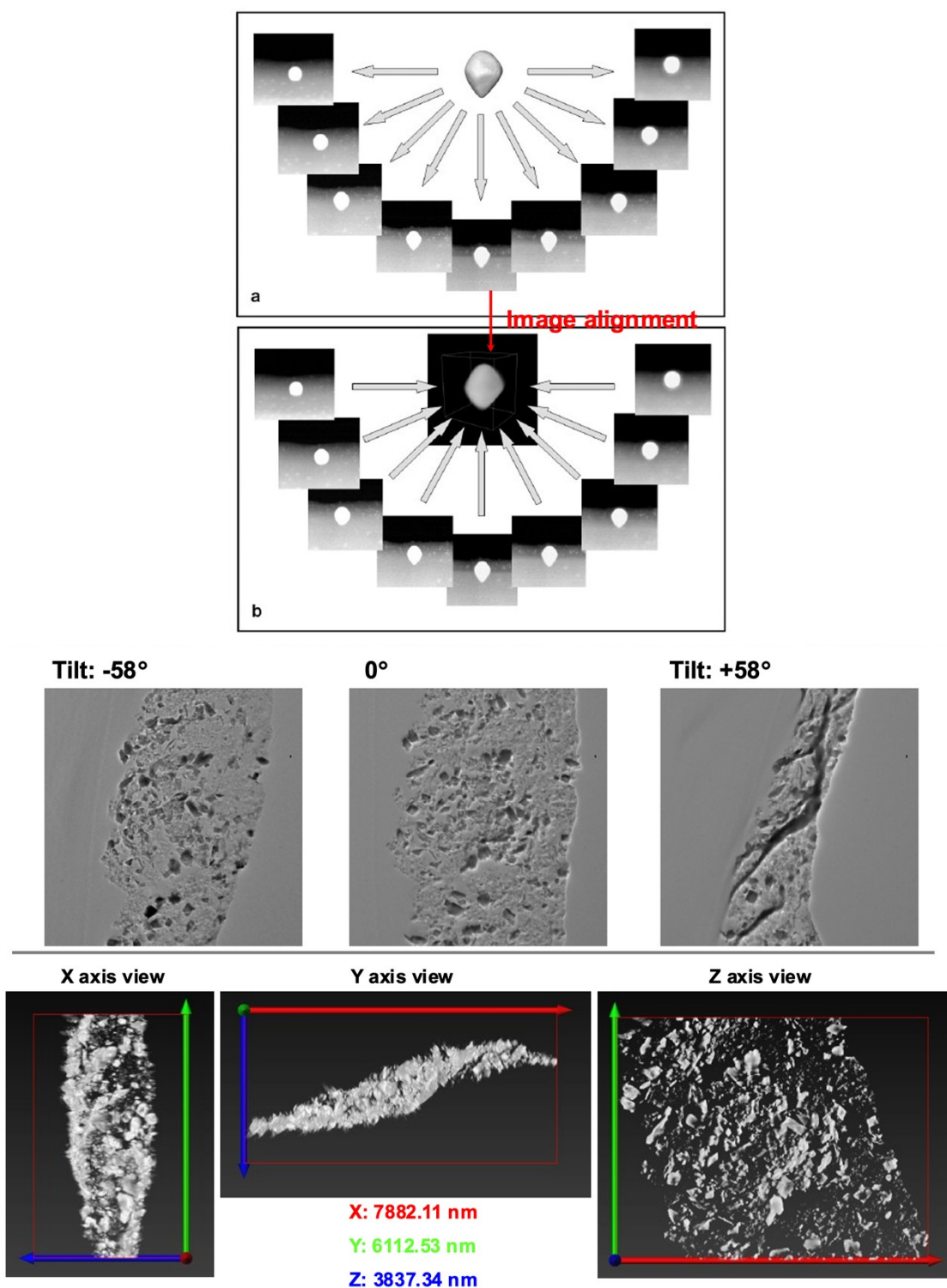


Figure S3. TEM tomography of composite FeOF electrode was conducted to examine the structure of the composite layer.

(a) Bare FeOF

Measured d spacing (Å)	FeOF (P4 ₂ /m n n m)	FeOF (P4 ₂ /m n n m)
2.48	2.556	(101)
2.13	2.081	(210)
1.52	1.529	(002)
1.23	1.23	(122)
ICSD #	2875	

(b) LiPON-coated- FeOF

Measured d spacing (Å)	Fe (Fm-3m)	Fe (Fm-3m)
2.083	2.1	(111)
1.8	1.823	(200)
1.29	1.289	(022)
ICSD #	44862	

Figure S4. d-spacing data from TEM electron diffraction after discharged to 1.2V vs. Li/Li⁺ for (a) Bare FeOF, and (b) LiPON-coated-FeOF,

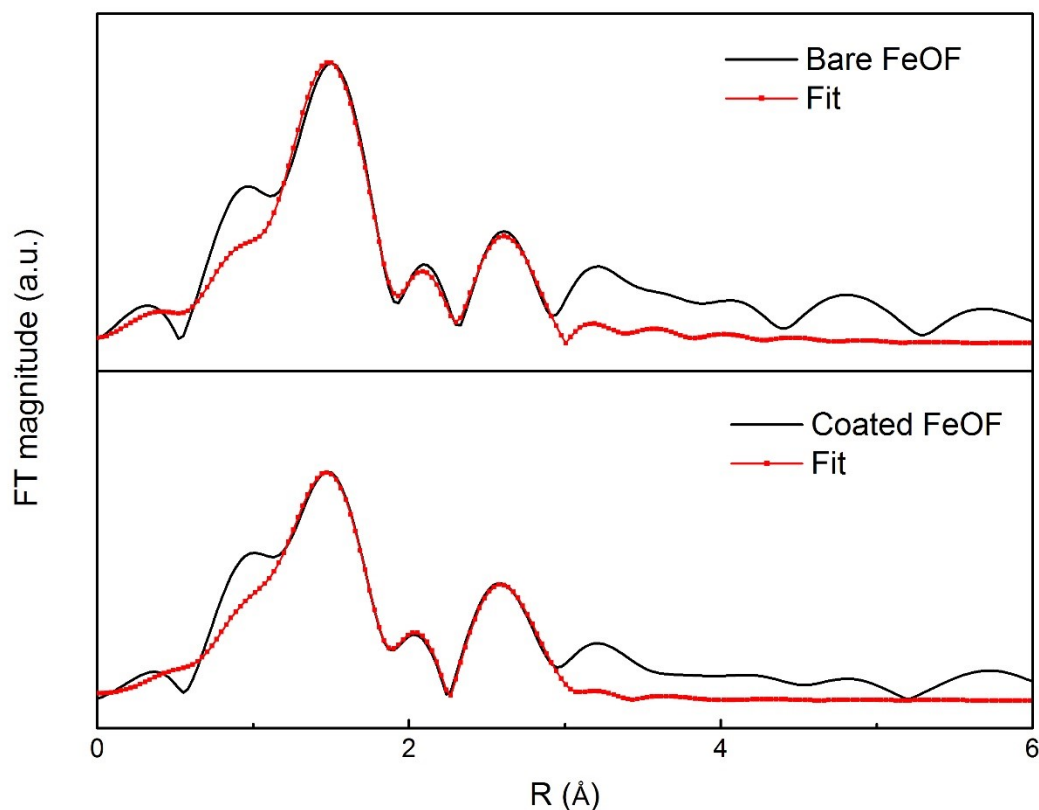


Table S1.					χ^2_r	R-factor
Sample	Path	R	ΔR	σ^2		
Bare FeOF	Fe-O	3.0 (2)	0.04 (2)	0.008 (2)	130.1	0.015
	Fe-F	2.7 (3)	0.03 (5)	0.015 (6)		
	Fe-Fe	1.6 (4)	-0.03 (4)	0.013 (4)		
Coated FeOF	Fe-O	6.0 (9)	0.06 (2)	0.009 (1)	159.0	0.011
	Fe-F	0.9 (6)	0.08 (4)	0.011 (4)		
	Fe-Fe	2.2 (2)	-0.04 (3)	0.012 (3)		

*Fitting was obtained with $S_0^2 = 0.81$ and $\Delta E_0 = -1.1\text{eV}$.

Figure S5. Fitted Fourier transformed k^3 -weighted EXAFS spectra for bare and coated FeOF at OCV condition. Details of fitting parameters can be found in Table S1.

Table S1. Structural parameters obtained from XAFS fitting. Fitting range was from $k=3$ to 11, with $dk=2$, and $R=1.1$ to 2.9. Numbers in parenthesis corresponds to uncertainty in the last digits of parameters.

In order to quantify the contribution of each bond in FeOF to RDF patterns, XAFS fitting was performed using Artemis program. Bare and coated FeOF at OCV were fitted, while lithiated samples were not investigated because without the help of in-situ XRD data, the distortion in structure caused by lithiation

led to increasingly poorer fitting as charging proceed, and the existence of multiple phases made fitting impractical - Maximum number of fitting parameter is limited to $\frac{2\Delta k \Delta R}{\pi} + 2$. The crystal structure of FeOF was obtained from ref. (Chevrier). This structure was calculated in theory based on minimal energy approach. In the crystal, octahedrally coordinated Fe site is distorted, slightly shifting toward to O atoms, giving rise to shorter path length Fe-O interaction (1.93 and 1.94 Å) than Fe-F (2.12 and 2.13 Å), as shown in figure 4(a). The detection limit of XAFS is given by $\delta R \sim \pi/2k_{max}$, which, in our case, with $k_{max} \sim 15.5$, leads to a spatial resolution of ~ 0.1 Å. Therefore, Fe-O and Fe-F interaction can be distinguished while the small splitting in Fe-O and Fe-F subshells is under the detection limit, and is not tracked by the fitting. As a consequence, the fitting was performed using three scattering paths, i.e. Fe-O, Fe-F, and Fe-Fe. The scattering paths were generated based on an ab-initio program FeFF8. The scattering amplitude and phase shift parameters from the atomic coordinate of model compound were also calculated.

In order to minimize the correlation between fitting parameters and reduce the total number of floating parameters, the fitting was first performed on a model material, an as-fabricated pristine FeOF. Single values of amplitude reduction factor (S_0^2) and energy shift (ΔE_0) are obtained and used for following fittings. The fitting was then performed on bare and coated FeOF at OCV condition. A summary of structural parameters obtained by fitting for both bare and coated FeOF is provided in Table S1. It can be seen that crystal structure of bare FeOF is in agreement with theory, with O/F ratio larger than 1. Interestingly, however, coated FeOF showed drastically different O/F ratio, with O much more than F. This suggests that F in the coated FeOF was partially removed. Previous studies have shown that PO_3^- A possible explanation is that, since LiPON is an amorphous material the under-coordinated phosphorous might have a strong tendency to fulfill its electronic structure, therefore obtaining F ions from FeOF or swapping F ions with N ions.

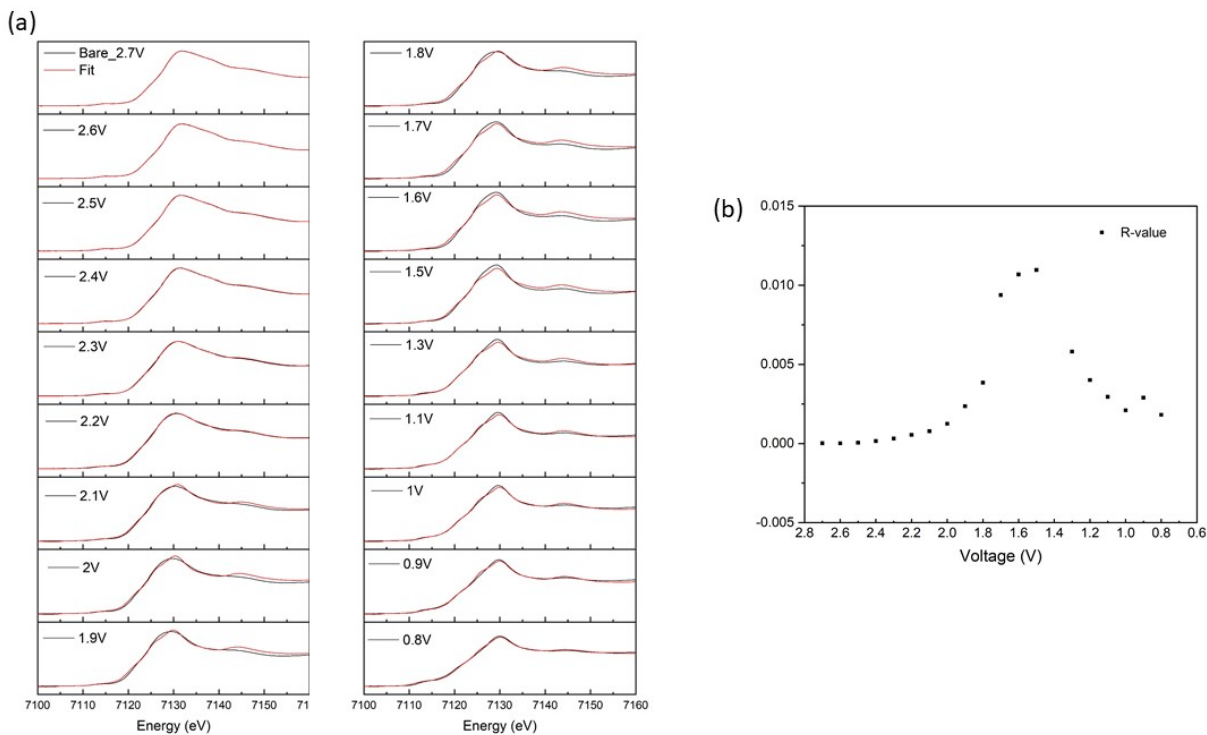


Figure S6. (a) LCA fitting for bare FeOF using BCC Fe metal, FeO, and Fe₂O₃ representing Fe⁰, Fe²⁺, and Fe³⁺ at different voltages; (b) the R-value of the fitting.

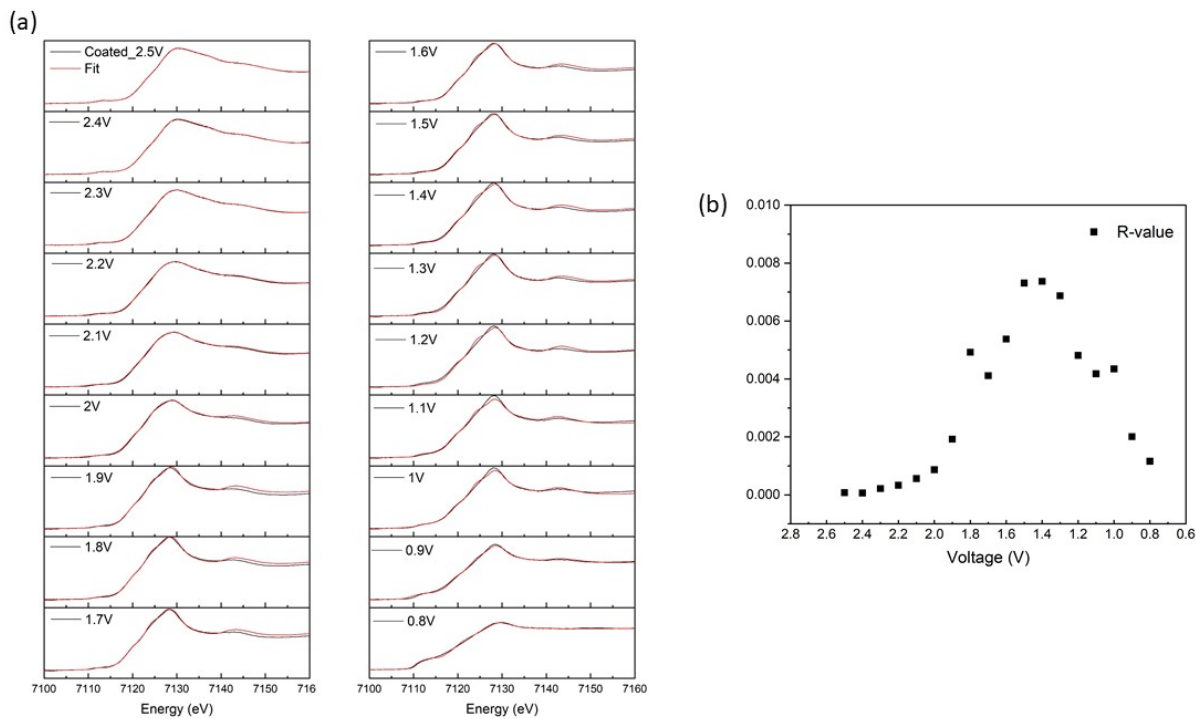


Figure S7. (a) LCA fitting for LiPON-coated-FeOF using BCC Fe metal, FeO, and Fe₂O₃ representing Fe⁰, Fe²⁺, and Fe³⁺ at different voltages; (b) the R-value of the fitting.