Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Ultrafast kinetics in a phase separating electrode material by forming an intermediate phase without reducing the particle size

Minkyung Kim[†‡], Mihee Jeong[§], Won-Sub Yoon[§], Byoungwoo Kang[†*]

[†]Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea

[‡] Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[§]Department of Energy Science, Sungkyunkwan University, Suwon, 440-746, Republic of Korea

Table S1. Lattice parameters of PTFE-$LiVPO_4F$ and CTR-$LiVPO_4F$ by Rietveld refinement

PTFE-$LiVPO_4F$

$P\bar{1}$; Z=2
a = 5.1835(4) Å, b = 5.3124(2) Å, c = 7.2672(2) Å
alpha = 107.582(3)°, beta = 107.955(2)°, gamma = 98.447(7)°
Volume = 175.007(8) Å^3

Bragg R-factor: 6.62
RF-factor : 5.17

Atomic Parameters

Atoms	Wyckoff position	x/a	y/b	z/c	Occ.	B_{iso}
V(1)	1a	0	0	0	1	0.404
V(2)	1b	0	0	0.5	1	0.306
P	2i	0.31889(90)	0.64652(87)	0.24986(83)	1	0.557
O(1)	2i	0.36980(177)	0.24044(148)	0.58599(137)	1	0.842
O(2)	2i	0.11048(186)	-0.32998(146)	0.36133(139)	1	0.299
O(3)	2i	0.68291(180)	0.66372(180)	-0.13847(125)	1	0.752
O(4)	2i	0.27067(157)	0.79328(152)	0.08892(129)	1	0.425
F	2i	-0.11871(137)	0.64652(87)	0.24535(117)	1	0.417
Li	2i	0.70771(656)	0.38817(593)	0.22343(476)	1	2.635

CTR-$LiVPO_4F$

$P\bar{1}$; Z=2
a = 5.1752(6) Å, b = 5.3086(7) Å, c = 7.2653(5) Å
alpha = 107.571(1)°, beta = 107.980(8)°, gamma = 98.354(4)°
Volume = 174.627(7) Å^3

Bragg R-factor: 7.33
RF-factor : 5.99

Atomic Parameters

Atoms	Wyckoff position	x/a	y/b	z/c	Occ.	B_{iso}
V(1)	1a	0	0	0	1	0.404
V(2)	1b	0	0	0.5	1	0.306
P	2i	0.31839(92)	0.64696(94)	0.25105(83)	1	0.557
O(1)	2i	0.36980(177)	0.24044(148)	0.58599(137)	1	0.842
O(2)	2i	0.11048(186)	-0.32998(146)	0.36133(139)	1	0.299
O(3)	2i	0.68980(190)	0.66587(193)	-0.13714(134)	1	0.752
O(4)	2i	0.27660(167)	0.78845(164)	0.08893(139)	1	0.425
F	2i	-0.11544(149)	0.09029(149)	0.24906(124)	1	0.417
Li	2i	0.70426(693)	0.39044(631)	0.20041(469)	1	2.635

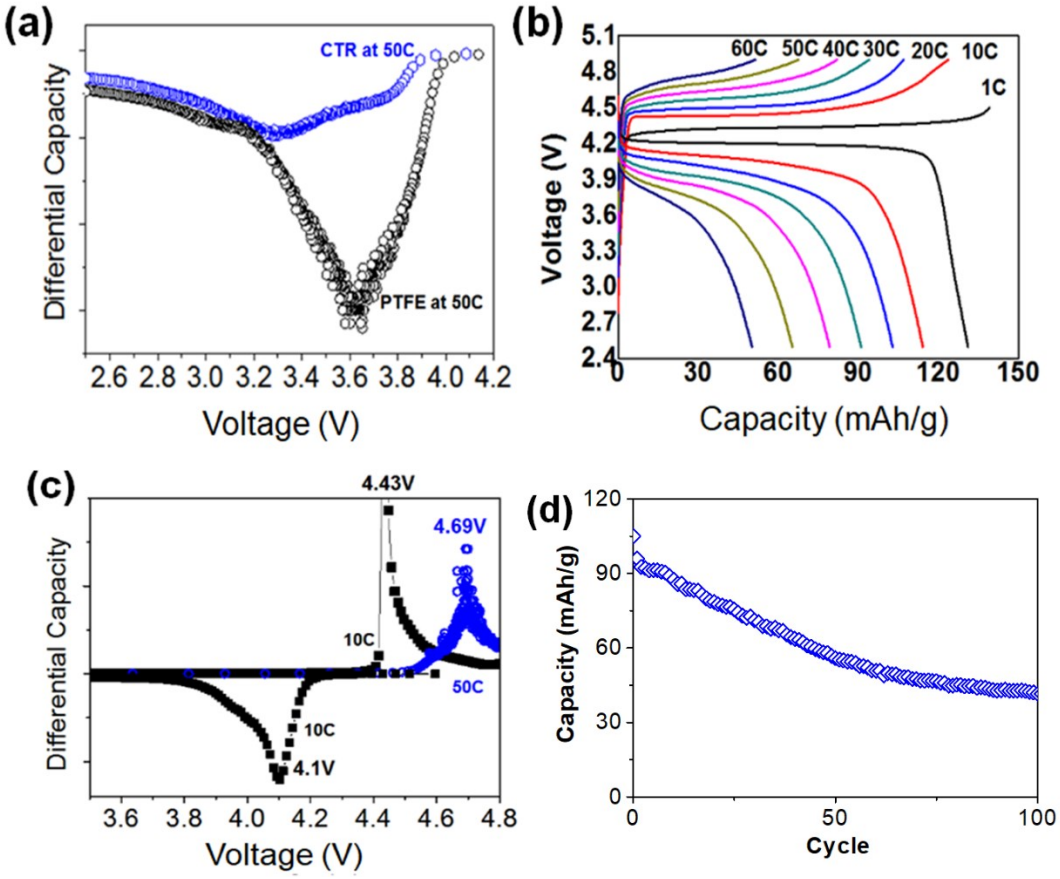


Figure S1. (a) Differential capacity plot of PTFE-$LiVPO_4F$ and CTR-$LiVPO_4F$ of **Figure 2a** and **2b** (a 50C discharge rate). Voltage polarization is much higher in CTR-$LiVPO_4F$ sample than the PTFE-$LiVPO_4F$. (b) Voltage profiles of **Figure 2e** of PTFE-$LiVPO_4F$ (c) Differential capacity plot (dQ/dV) of (b) at a 10C and 50C charge rate. (d) Cycle retention of CTR-$LiVPO_4F$. It was charged and discharged at 1C rate (4.5-3V).

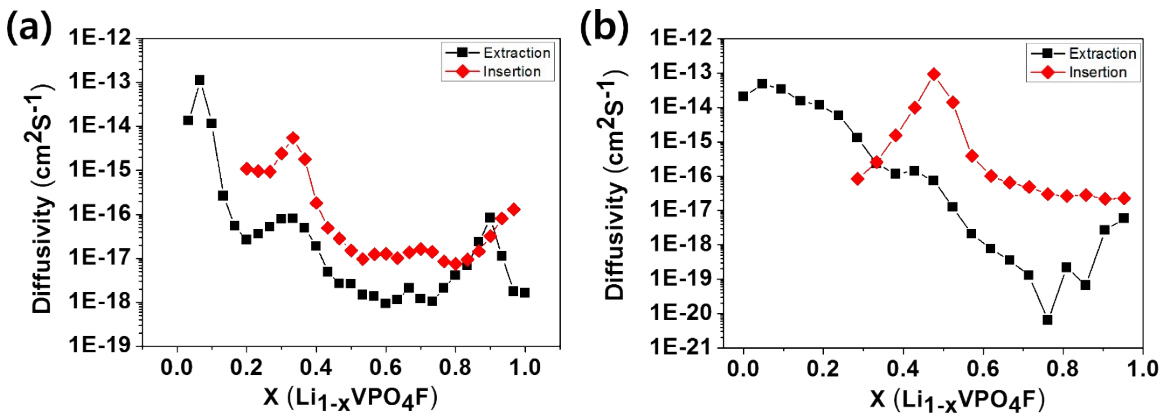


Figure S2. Calculated Li ion diffusivity from galvanostatic intermittent titration technique (GITT) method of (a) PTFE-$LiVPO_4F$ and (b) CTR-$LiVPO_4F$.

This calculation was based on the below equation (1) developed by Weppner et. al.

$$D_{Li^+} = \frac{4}{\pi}\left(\frac{V_M}{SF}\right)^2\left(I_0\frac{\delta E_s/\delta x}{\delta E/\delta t^{1/2}}\right)^2 \quad \text{at } t \ll \tau \quad \text{------- (1)}$$

where V_M is molar volume 5.2346×10^{-5} m^3/mol, S is the electrode surface area of each samples, F is the Faraday's constant 96,485.3365 C/mol, I_0 is the pulse current, $\delta Es/\delta x$ is the slope of equilibrium open circuit voltage (OCV) with respect to Li amount, which can be obtained from the differential of OCV curve, and $\delta E/\delta t^{1/2}$ is the slope of initial transient voltage change with respect to square root of time.

The diffusivities are changed depending on the lithium composition in both samples, PTFE-$LiVPO_4F$ and CTR-$LiVPO_4F$. In both $LiVPO_4F$ samples, carbon was included with $LiVPO_4F$, so the surface area of the composite sample ($LiVPO_4F$ + carbon) was considered. The measured Li diffusivity of PTFE-$LiVPO_4F$ was compared with the reported Li diffusivity of $LiVPO_4F$ by P.F. Xiao et. al.[1] The range of the two diffusivities are similar to each other.

Table S2. Electronic conductivities of the composite samples that have $LiVPO_4F$ and carbon. Each sample was pelletized, and then Ag paste was put on the top and bottom of the pellets. Direct current (DC) measurement was conducted to the pellets with stainless collector.

PTFE-$LiVPO_4F$	**CTR-$LiVPO_4F$**
9.0×10^{-3} S/cm	**6.4×10^{-3} S/cm**

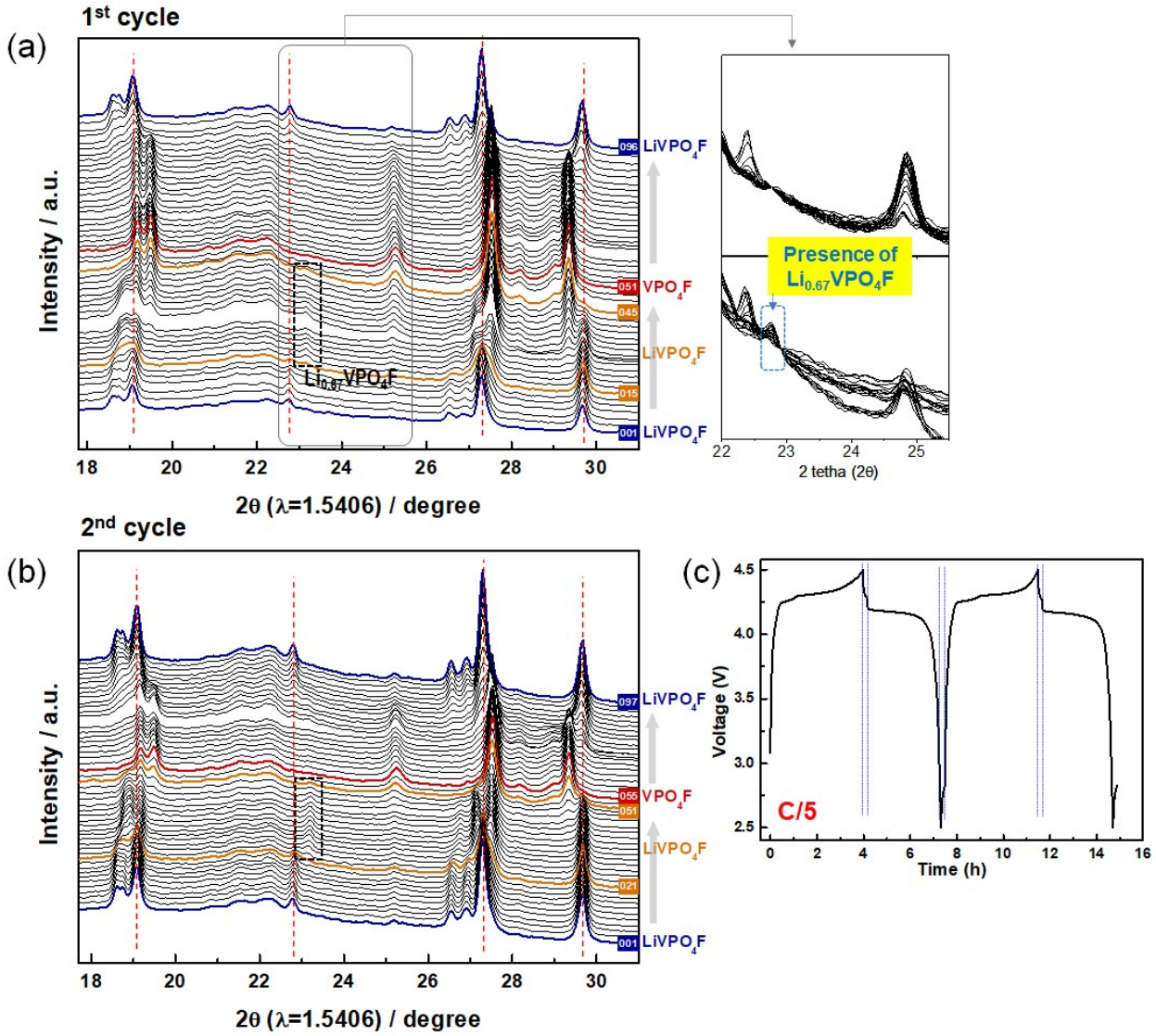
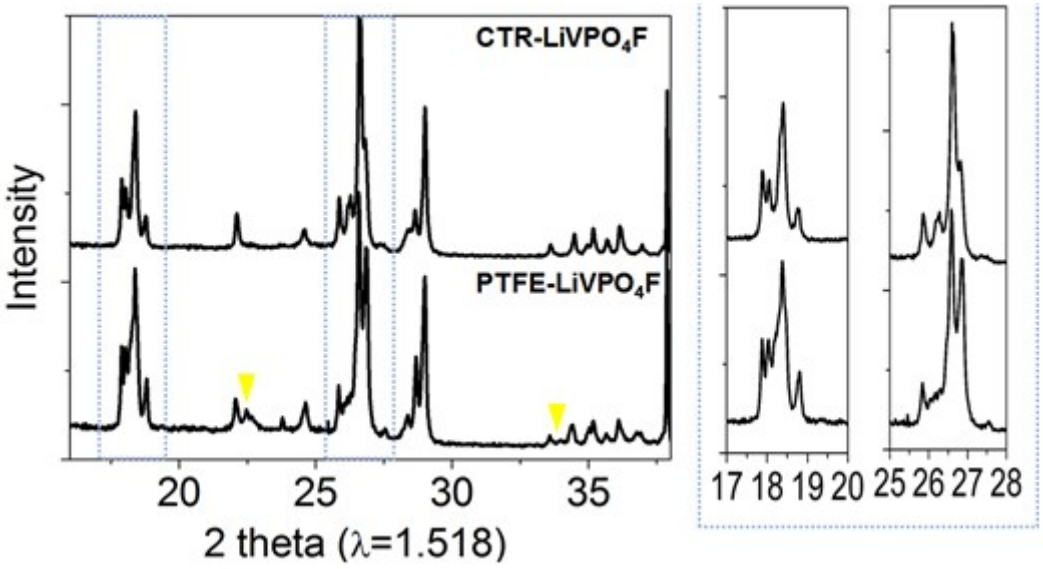


Figure S3. Operando synchrotron XRD patterns of CTR-$LiVPO_4F$ for 2 cycles. XRD diffraction patterns represent at (b) 1st cycle and (c) 2nd cycle. Red dash vertical lines indicate main peaks of $LiVPO_4F$. (c) its voltage profile for 2 cycles. It was charged at C/5 rate and discharged at C/5 rate. The cell was rested for 10 mins after each step during charge/discharge (blue dash vertical lines)



F**igure S4**. High resolution powder synchrotron XRD patterns of *ex situ* electrodes of CTR-$LiVPO_4F$ and PTFE-$LiVPO_4F$ at DOD50 (Depth of Discharge 50%), which is a $Li_{0.5}VPO_4F$ with the lithiation, at a C/5 rate.(▼: $Li_{0.67}VPO_4F$). Main peak shapes were different due to the introduction of the intermediate phase.

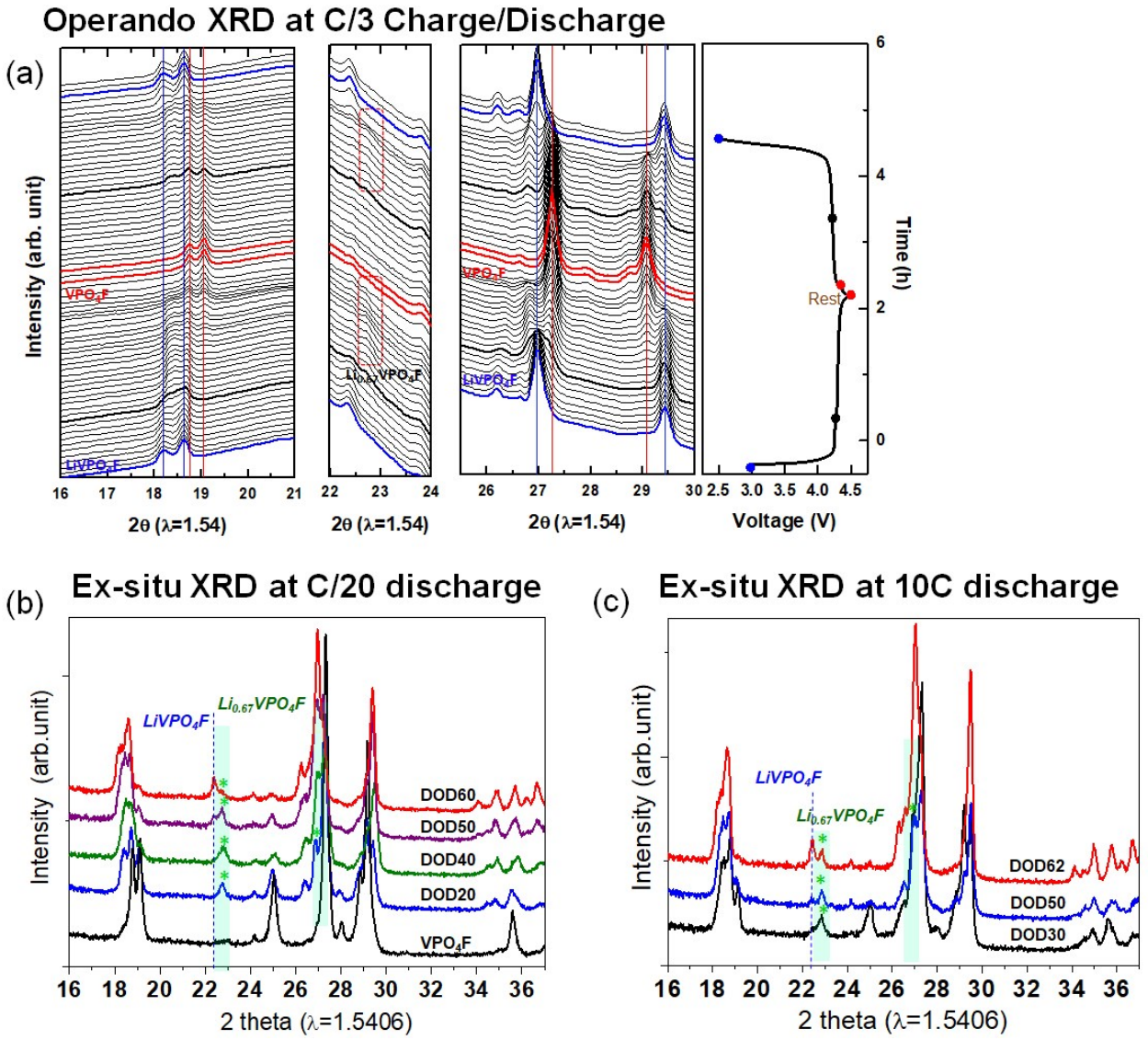


Figure S5. Phase transformation behaviors in PTFE-$LiVPO_4F$ at various C-rates (a) Operando synchrotron XRD patterns at C/3 charge rate and C/3 discharge rate and its voltage profile. *Ex situ* XRD patterns at (b) C/20 discharge rate and (c) 10C discharge rate. Both cells were charged at C/5 rate. Depth of Discharge (DOD) was described on each XRD pattern.

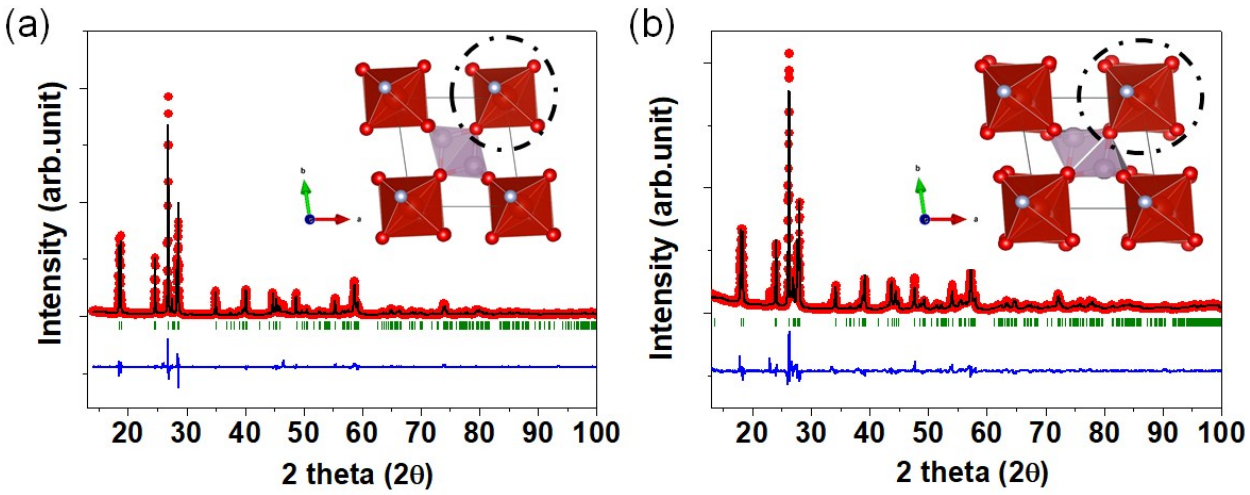


Figure S6. Synchrotron XRD patterns of chemically delithiated (a) CTR-VPO_4F and (b) PTFE-VPO_4F. Monoclinic VPO_4F structure is converted to triclinic with assuming VPO_4F forms by fully extracting Li ions from triclinic $LiVPO_4F$. Rietveld refinement was conducted using triclinic VPO_4F. More details are our previous study.[2] Based on the calculation, the dihedral angle of VO_4F_2 octahedra in VPO_4F can be an indicator for the amount of the oxygen defects in the materials. The dihedral angle of VO_4F_2 octahedra in VPO_4F is ~ 2.2° and ~ 4° for experimentally synthesized CTR-VPO_4F and PTFE-VPO_4F, respectively. This indicates that PTFE-$LiVPO_4F$ can have less amount of the oxygen defects than CTR-$LiVPO_4F$

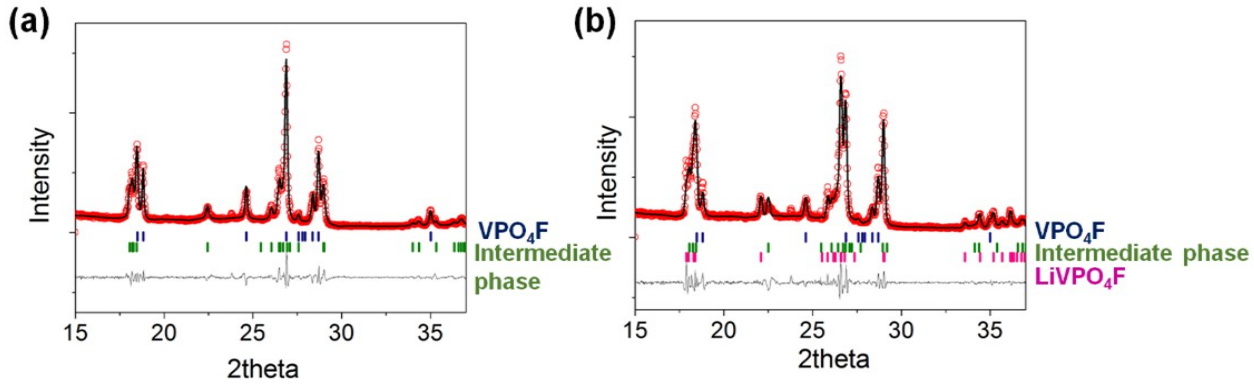


Figure S7. Synchrotron XRD patterns of *ex situ* electrodes of PTFE-$LiVPO_4F$ at (a) DOD20, which is a $Li_{0.2}VPO_4F$ with the lithiation of 20 % Li, and (b) DOD50, which is a $Li_{0.5}VPO_4F$ with the lithiation of 50 % Li. These XRD patterns were analyzed by a profile matching. Red dots represent an observed data, black lines represents the theoretical Bragg patterns of the phases. Gray line is the difference between the observed pattern and the theoretical one. (R-factor: 5.89, Chi^2: 4.04 in (a), R-factor: 5.53, Chi^2: 4.57 in (b))

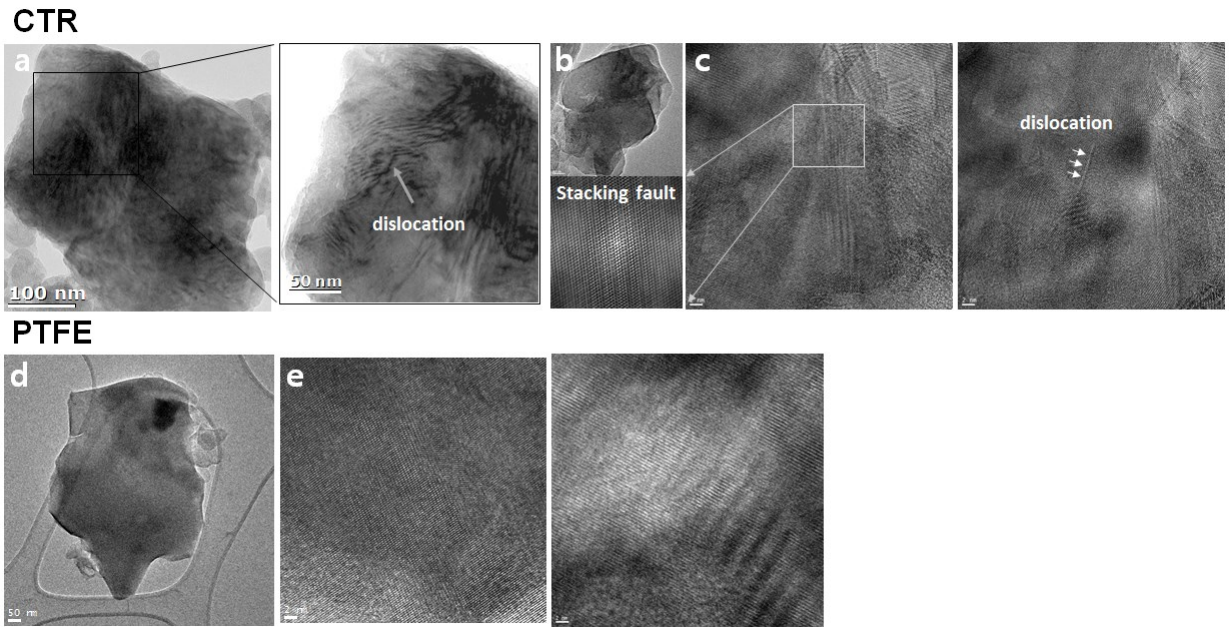


Figure S8. TEM measurements of particles in electrochemically lithiated two samples with DOD50. Structural analyses of the CTR-$Li_{0.5}VPO_4F$ (a) Low magnification image with its enlarged image of the dislocation part, (b) Low magnification image and (c) its high resolution image of stacking faults and dislocations. Structural analyses of the PTFE-$Li_{0.5}VPO_4F$ (d) Low magnification image and (c) its high resolution image. Much more structural defects such as stacking faults and dislocations are observed in the CTR-$LiVPO_4F$ than the PTFE-$LiVPO_4F$.

Reference

1. P. F. Xiao, M. O. Lai and L. Lu, *Solid State Ionics*, 2013, **242**, 10-19.
2. H. Park, M. Kim, S. Kang and B. Kang, *Journal of Materials Chemistry A*, 2019, **7**, 13060-13070.