Electronic supplementary information

Facile Lithium Ion Transport through Super-ionic Pathways Formed on the Surface of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ for High Power Li Ion Battery

Dong-Wook Han,[†] Sung-Jin Lim,[†] Yong-Il Kim,[‡] Seung Ho Kang,[§] Yoon Cheol Lee,[§] and Yong-Mook Kang^{*,§}

[†] Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Yuseong, Daejeon 305-701, Republic of Korea.

[‡] Korea Research Institute of Standards and Science, P.O. Box102, Yuseong, Daejeon 305-340, Republic of Korea

[§] Department of Energy and Materials Engineering, Dongguk University-Seoul, Seoul 100-715, Republic of Korea, E-mail: dake1234@dongguk.edu

Figure S1. (a) P 2p and (b) O 1s X-ray photoelectron spectroscopy (XPS) partial spectra for the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite compensated by the peak binding energy of the measured C 1s XPS spectra.

Figure S2. STEM image and EDS/EELS results for $\text{Li}_3\text{V}_{1.95}\text{Zr}_{0.05}(\text{PO}_4)_3/\text{C}$ and $\text{Li}_3\text{V}_{1.9}\text{Zr}_{0.1}(\text{PO}_4)_3/\text{C}$ composites.

Figure S3. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns of the $\text{Li}_3\text{V}_{1.95}\text{Zr}_{0.05}(\text{PO}_4)_3/\text{C}$ composites observed from surface to bulk.

Figure S4. SEM micrographs of the (a) $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$, (b) $\text{Li}_3\text{V}_{1.95}\text{Zr}_{0.05}(\text{PO}_4)_3/\text{C}$, and (c) $\text{Li}_3\text{V}_{1.9}\text{Zr}_{0.1}(\text{PO}_4)_3/\text{C}$ composites. (d) Particle size distribution of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ measured by particle size analyzer (PSA).

Figure S5. Galvanostatic (0.2 C, 1 C = 197 mA h g^{-1}) voltage profiles of the $\text{Li}_3\text{V}_{2-x}\text{Zr}_x(\text{PO}_4)_3/\text{C}$ measured after 1st, 10th, 20th, 30th, 40th, and 50th cycles.

Figure S6. (a) *Ex-situ* XRD patterns for the $\text{Li}_3\text{V}_{2-x}\text{Zr}_x(\text{PO}_4)_3/\text{C}$ ($x = 0, 0.05, 0.1$) composites after 50 cycles at 0.2 C in the voltage range of 3.0-4.8V and (b) Rietveld refinement patterns of $\text{Li}_3\text{V}_{1.95}\text{Zr}_{0.05}(\text{PO}_4)_3$ using X-ray powder diffraction data, after 50 cycles at 0.2 C in the voltage range of 3.0-4.8V. Plus marks (+) represent the observed intensities, and the red solid line is calculated result. The difference plot (blue) is shown at the bottom. Tick marks above the difference plot indicate the reflection positions (top: $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, bottom: $\text{LiZr}_2(\text{PO}_4)_3$).

Site	x/a	y/b	z/c	Occupation	$B_{eq}/\text{\AA}^2$
Li1	0.2928(2)	0.3238(3)	0.2887(3)	1.0	2.08(1)
Li2	0.9347(2)	0.2354(2)	0.3158(2)	1.0	0.72(2)
Li3	0.5810(2)	0.1910(2)	0.3945(3)	1.0	0.73(2)
V1	0.2496(1)	0.1096(2)	0.4620(2)	1.0	0.05(2)
V2	0.7507(3)	0.3896(2)	0.4721(2)	1.0	0.24(3)
P1	0.1067(2)	0.1484(3)	0.1040(2)	1.0	0.25(3)
P2	0.6057(3)	0.3533(3)	0.1155(3)	1.0	0.52(2)
P3	0.0363(3)	0.4915(3)	0.2479(3)	1.0	0.13(2)
O1	0.4303(2)	0.3307(3)	0.0902(2)	1.0	0.41(3)
O2	0.9239(1)	0.1507(3)	0.1152(3)	1.0	0.39(4)
O3	0.3551(2)	0.2619(2)	0.4812(2)	1.0	0.51(2)
O4	0.8018(2)	0.2196(3)	0.4918(3)	1.0	0.10(2)
O5	0.6451(2)	0.4781(3)	0.0845(2)	1.0	0.90(3)
O6	0.1762(2)	0.0393(3)	0.0498(3)	1.0	0.93(5)
O7	0.4563(2)	0.0681(3)	0.3675(1)	1.0	0.55(4)
O8	0.9310(1)	0.4024(2)	0.3215(2)	1.0	1.26(3)
O9	0.1669(2)	0.4286(2)	0.1653(3)	1.0	0.44(1)
O10	0.6129(2)	0.0727(2)	0.1350(1)	1.0	1.20(4)
O11	0.1648(2)	0.1863(3)	0.2691(2)	1.0	1.18(4)
O12	0.6394(2)	0.3165(2)	0.2895(1)	1.0	0.74(1)

Space group: P1121/n (No. 14)

Number of formula units (Z): 4

$a = 8.6117(2) \text{ \AA}$, $b = 12.0483(2) \text{ \AA}$, $c = 8.5993(2) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 90.56(1)^\circ$

$R_{wp} : 8.41$ $R_p : 6.33$ $R_e : 6.15$ Goodness of fit ($S = R_{wp}/R_e$): 1.37

Table S1. Space group, lattice parameters, and atomic positions of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite obtained from the Rietveld refinement results, before cycling.

Site	x/a	y/b	z/c	Occupation	$B_{eq}/\text{\AA}^2$
Li1	0.2982(2)	0.3285(2)	0.2887(2)	1.0	1.44(1)
Li2	0.9401(3)	0.2226(2)	0.3192(2)	1.0	1.34(2)
Li3	0.6010(2)	0.1922(2)	0.3964(2)	1.0	1.43(2)
Zr1	0.2504(2)	0.1096(2)	0.4603(2)	0.0276(2)	0.43(2)
V1	0.2504(2)	0.1096(2)	0.4603(2)	0.9724(2)	0.43(2)
V2	0.7514(2)	0.3908(3)	0.4718(2)	1.0	0.39(3)
P1	0.1042(3)	0.1478(2)	0.1026(2)	1.0	0.42(2)
P2	0.6047(2)	0.3539(3)	0.1158(2)	1.0	0.46(2)
P3	0.0375(2)	0.4906(3)	0.2464(2)	1.0	0.34(3)
O1	0.4321(2)	0.3329(2)	0.0930(2)	1.0	1.04(2)
O2	0.9226(2)	0.1503(2)	0.1191(2)	1.0	0.84(3)
O3	0.3495(2)	0.2637(1)	0.4809(2)	1.0	0.75(1)
O4	0.8050(2)	0.2222(2)	0.4806(2)	1.0	1.14(1)
O5	0.6434(2)	0.4774(2)	0.0885(2)	1.0	1.79(1)
O6	0.1738(2)	0.0434(3)	0.0494(2)	1.0	1.19(3)
O7	0.4513(3)	0.0671(2)	0.3674(2)	1.0	1.51(2)
O8	0.9298(3)	0.3957(2)	0.3222(1)	1.0	1.78(2)
O9	0.1700(2)	0.4301(2)	0.1648(1)	1.0	0.86(1)
O10	0.6081(2)	0.0731(2)	0.1355(1)	1.0	1.12(3)
O11	0.1722(2)	0.1886(2)	0.2681(1)	1.0	0.89(2)
O12	0.6446(2)	0.3153(2)	0.2906(2)	1.0	1.54(2)

Space group: P1121/n (No. 14)

Number of formula units (Z): 4

$a = 8.6142(1) \text{ \AA}$, $b = 12.0505(2) \text{ \AA}$, $c = 8.6008(2) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 90.55(2)^\circ$

$R_{wp} : 7.73$ $R_p : 5.52$ $R_a : 5.07$ Goodness of fit ($S = R_{wp}/R_a$): 1.52

Table S2. Space group, lattice parameters, and atomic positions of the $\text{Li}_3\text{V}_{1.95}\text{Zr}_{0.05}(\text{PO}_4)_3/\text{C}$ composite obtained from the Rietveld refinement results, before cycling.

Compounds	Residual carbon content (% wt)	Electronic conductivity at R. T. (S cm^{-1})
$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	0.34	1.8×10^{-8}
$\text{Li}_3\text{V}_{1.95}\text{Zr}_{0.05}(\text{PO}_4)_3/\text{C}$	0.45	1.0×10^{-8}
$\text{Li}_3\text{V}_{1.8}\text{Zr}_{0.1}(\text{PO}_4)_3/\text{C}$	0.56	$< 1.0 \times 10^{-8}$ (Not to be measured)

Table S3. Residual carbon content and electronic conductivity of the $\text{Li}_3\text{V}_{2-x}\text{Zr}_x(\text{PO}_4)_3/\text{C}$ ($x = 0, 0.05, 0.1$) composites.

Site	x/a	y/b	z/c	Occupation	$B_{eq}/\text{\AA}^2$
Li1	0.2960(1)	0.2791(2)	0.4191(1)	1.0	1.24(1)
Li2	0.8361(1)	0.2033(2)	0.3952(1)	1.0	1.44(2)
Li3	0.6041(1)	0.2338(1)	0.3941(1)	1.0	1.34(2)
Zr1	0.2499(1)	0.1135(2)	0.4651(1)	0.0235(2)	0.52(3)
V1	0.2499(1)	0.1135(2)	0.4651(1)	0.9765(2)	0.52(3)
V2	0.7587(1)	0.3858(2)	0.4675(1)	1.0	0.36(2)
P1	0.1055(2)	0.1441(1)	0.1171(2)	1.0	0.42(3)
P2	0.6104(2)	0.3509(1)	0.1204(2)	1.0	0.46(2)
P3	0.0367(2)	0.4911(1)	0.2341(2)	1.0	0.34(2)
O1	0.4629(2)	0.3427(2)	0.0859(1)	1.0	1.04(2)
O2	0.9238(2)	0.1537(2)	0.1247(2)	1.0	0.84(3)
O3	0.3486(3)	0.2774(3)	0.5061(3)	1.0	0.75(2)
O4	0.8250(3)	0.2454(2)	0.5041(3)	1.0	1.14(1)
O5	0.6000(2)	0.4874(2)	0.0629(2)	1.0	2.79(1)
O6	0.1572(2)	0.0492(2)	0.0677(2)	1.0	1.19(1)
O7	0.4724(2)	0.0619(2)	0.3457(2)	1.0	1.51(1)
O8	0.9417(3)	0.4125(2)	0.3586(2)	1.0	1.78(2)
O9	0.1641(3)	0.4252(1)	0.1790(1)	1.0	0.86(1)
O10	0.6479(2)	0.0792(2)	0.1680(2)	1.0	1.12(2)
O11	0.1925(3)	0.1981(2)	0.2630(2)	1.0	0.89(1)
O12	0.6280(1)	0.3302(2)	0.2821(1)	1.0	1.54(2)

Space group: P1121/n (No. 14)

Number of formula units (Z): 4

$a = 8.6140(1) \text{ \AA}$, $b = 12.0500(3) \text{ \AA}$, $c = 8.6006(1) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 90.55(2)^\circ$

$R_{wp} : 7.72$ $R_p : 5.86$ $R_e : 6.09$ Goodness of fit ($S = R_{wp}/R_e$): 1.40

Table S4. Space group, lattice parameters, and atomic positions of the $\text{Li}_3\text{V}_{1.95}\text{Zr}_{0.05}(\text{PO}_4)_3/\text{C}$ composite obtained from the Rietveld refinement results, after 50 cycles at 0.2 C in the voltage range of 3.0-4.8V.

Compounds	$R_{ct,LVP}$ ($\Omega \text{ cm}^2$)	$R_{ct,Li}$ ($\Omega \text{ cm}^2$)	R_s ($\Omega \text{ cm}^2$)
$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$	621.4	381.7	2.583
$\text{Li}_3\text{V}_{1.95}\text{Zr}_{0.05}(\text{PO}_4)_3/\text{C}$	439.4	164.6	2.763
$\text{Li}_3\text{V}_{1.9}\text{Zr}_{0.1}(\text{PO}_4)_3/\text{C}$	567.9	214.3	1.099

Table S5. Resistances ($R_{ct,LVP}$, $R_{ct,Li}$, and R_s) obtained from electrochemical impedance spectroscopy (EIS) spectra of the $\text{Li}_3\text{V}_{2-x}\text{Zr}_x(\text{PO}_4)_3/\text{C}$ ($x = 0, 0.05, 0.1$) composites measured after cell formation, fitted using an equivalent circuit model.