Supporting Information

Structural Impact of Zn-insertion into Monoclinic $V_2(PO_4)_3$: Implications for Zn-ion Batteries

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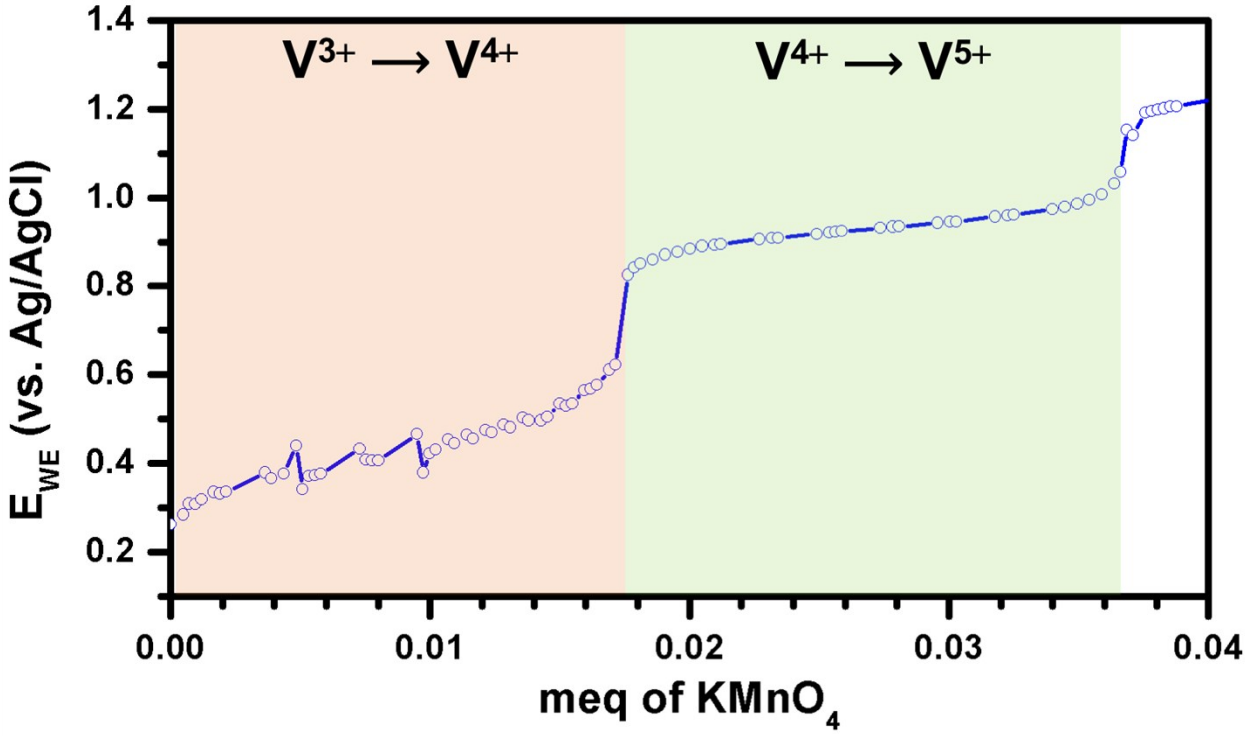

Fig. S1 Potential measured against equivalent volume of $KMnO_4$ for the redox titration of Zn-inserted $V_2(PO_4)_3$ obtained via microwave irradiation at 140 °C for 10 min.

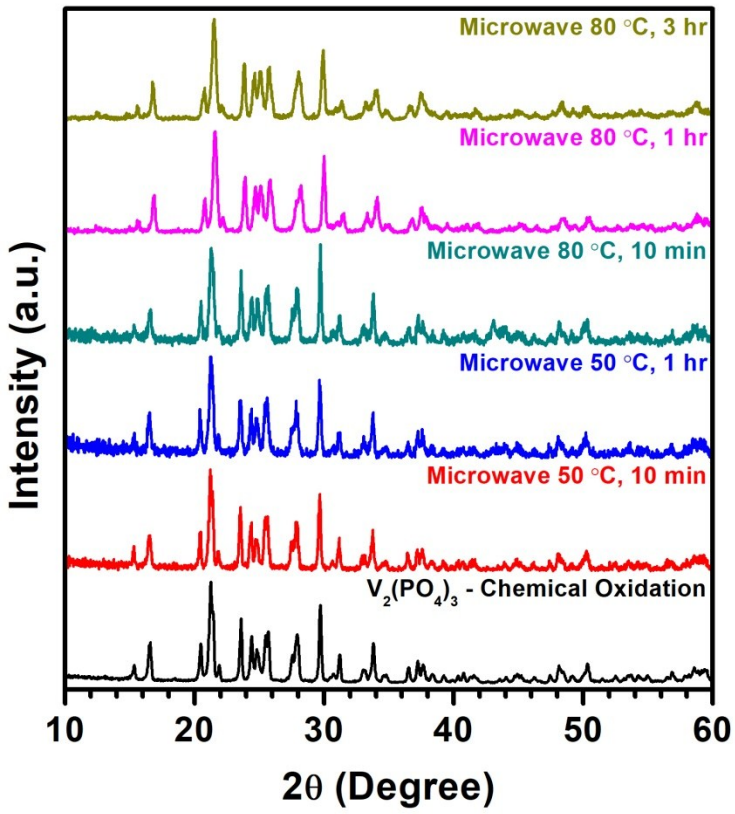

Fig. S2 XRD patterns of $V_2(PO_4)_3$ before microwave irradiation, after microwave irradiation at 50 °C for 10 min and 1 h, and after microwave irradiation at 80 °C for 10 min, 1 h, and 3 h.

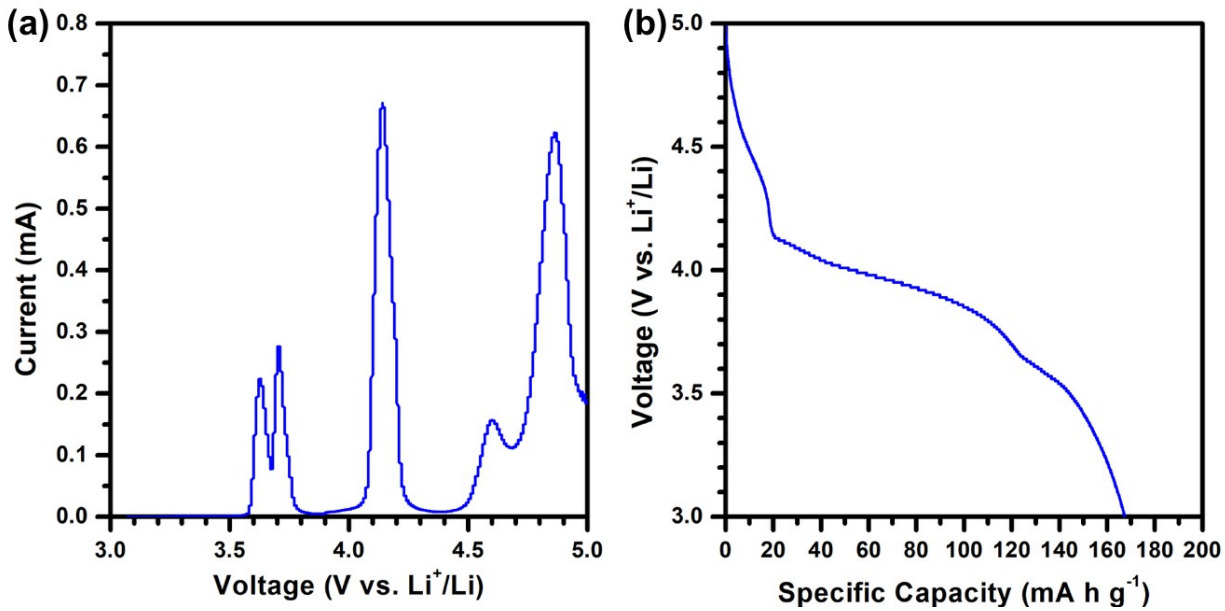

Fig. S3 (a) Linear sweep voltammetry (LSV) of $Li_3V_2(PO_4)_3$ electrode for electrochemical preparation of $V_2(PO_4)_3$ and (b) discharge profile of the electrode after the LSV step.

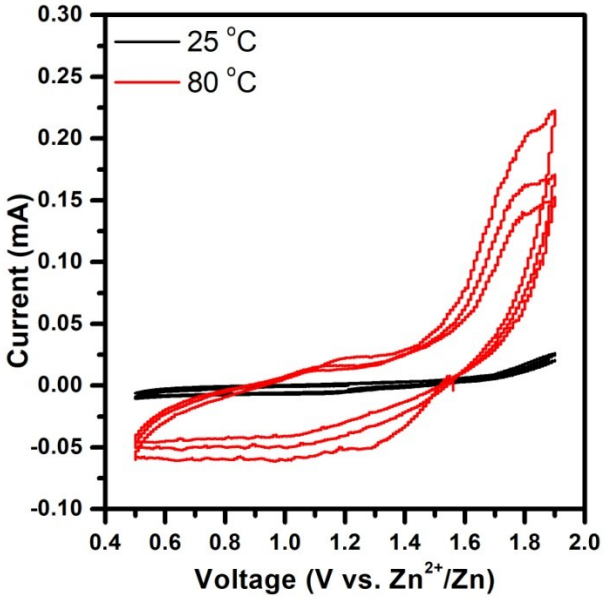

Fig. S4 Cyclic voltammetry (CV) of $V_2(PO_4)_3$ electrode at 25 °C (black) and 80 °C (red).

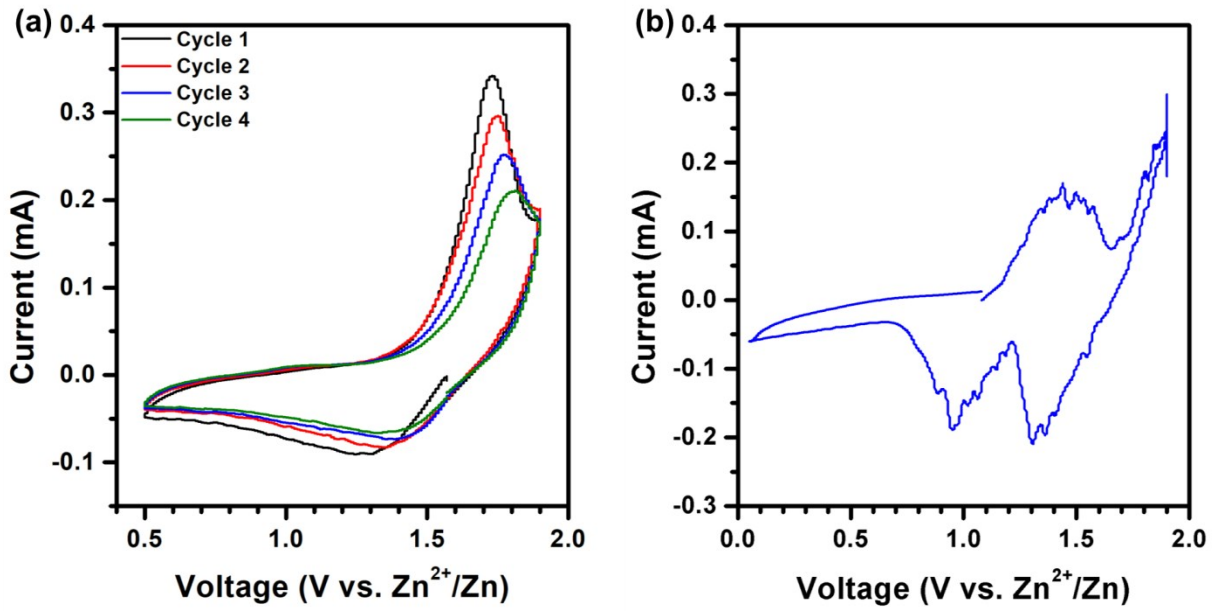

Fig. S5 CV of (a) $LiV_2(PO_4)_3$ electrode and (b) $Li_3V_2(PO_4)_3$ electrode in non-aqueous Zn-ion set-up.

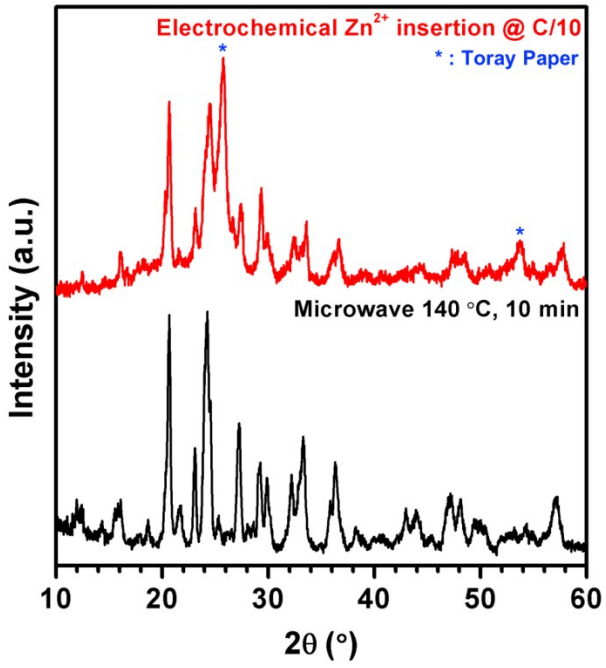

Fig. S6 XRD patterns of Zn-inserted $V_2(PO_4)_3$ via microwave-irradiation (black) and $V_2(PO_4)_3$ electrode after electrochemical Zn-insertion (red) (*: Peaks due to Toray paper).

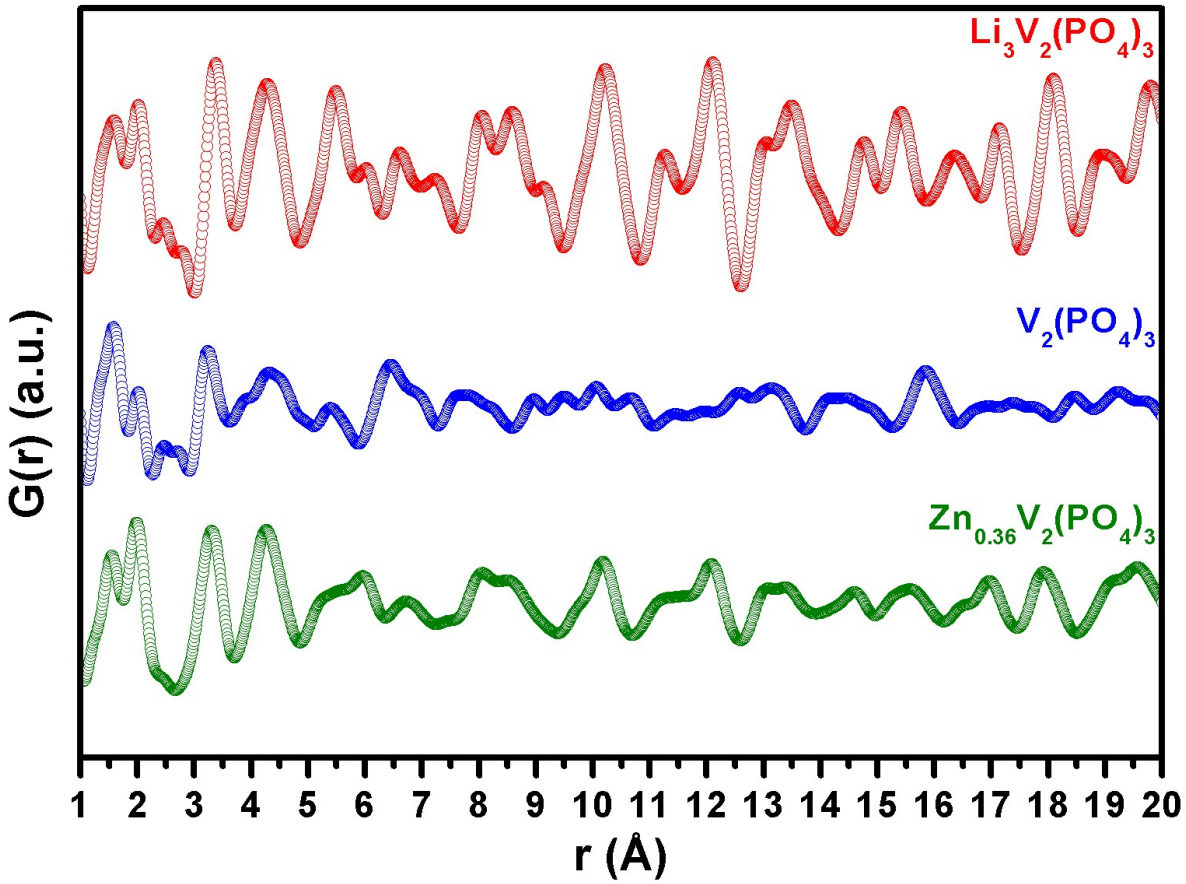

Fig. S7 Observed PDF curves of $Li_3V_2(PO_4)_3$ (top), $V_2(PO_4)_3$ (middle), and $Zn_{0.36}V_2(PO_4)_3$ (bottom) in the range of 1 to 20 Å.

Table S1 Refined cell parameters and statistics, atomic coordinates, and isotropic thermal parameters obtained from Rietveld refinement of the powder XRD of $V_2(PO4)_3$ prepared *via* chemical oxidation

Refined Cell Parameters and Statistics
Space Group : P 2_1/c a = 8.3058(7) Å; b = 8.58721(9) Å; c = 14.02173(7) Å; $\alpha = \gamma$ = 90.0000 °; β = 125.663(9) ° V = 812.52(5) Å^3 R_{wp} = 11.008 %; R_F^2 = 4.681 %

Atomic Coordinates

Label	x	y	z	U_{iso} (Å^2)	Fractions	Site
V1	0.3736(3)	0.46588(4)	0.11718(5)	0.012018(4)	1	4e
V2	0.13433(6)	0.4708(3)	0.38658(7)	0.01(2)	1	4e
P1	0.25922(3)	0.11785(5)	0.14878(3)	0.016616(5)	1	4e
P2	0.037(4)	0.6(1)	0.143(5)	0.016(6)	1	4e
P3	0.54312(7)	0.251(6)	0.00590(9)	0.016616(5)	1	4e
O1	0.11384(6)	0.08264(7)	0.17768(9)	0.0063040(5)	1	4e
O2	0.43921(1)	0.00892(9)	0.21929(9)	0.0063040(5)	1	4e
O3	0.15709(3)	0.07947(3)	0.01980(7)	0.0063040(5)	1	4e
O4	0.30249(2)	0.2940(7)	0.1605(3)	0.0063040(5)	1	4e
O5	0.173(9)	0.600(1)	0.106(6)	0.0063040(5)	1	4e
O6	0.104(8)	0.490(2)	0.241(8)	0.0063040(5)	1	4e
O7	0.183(3)	0.088(9)	0.455(4)	0.0063040(5)	1	4e
O8	0.055(1)	0.771(7)	0.193(7)	0.006(3)	1	4e
O9	0.55540(4)	0.32259(8)	0.11224(2)	0.0063040(5)	1	4e
O10	0.37451(5)	0.35090(2)	0.4383(1)	0.0063040(5)	1	4e
O11	0.54495(6)	0.12182(9)	0.42613(5)	0.0063040(5)	1	4e
O12	0.73979(4)	0.1657(3)	0.05686(4)	0.0063040(5)	1	4e

Table S2 Elemental ratio determined via ICP measurement of $LiV_2(PO_4)_3$ electrode after first reduction and subsequent oxidation in a Zn-ion cell

	Elemental ratio (per 2 V atoms)	
	After 1st reduction	After subsequent oxidation
Li : V	1.14	0.38
Zn : V	0.79	0.58

Table S3 Refined cell parameters and statistics, atomic coordinates, and isotropic thermal parameters obtained from Rietveld refinement of the powder XRD of $Zn_{0.36}V_2(PO4)_3$ prepared *via* microwave-assisted chemical insertion

Refined Cell Parameters and Statistics						
Space Group : P 2_1/c a = 8.508(7) Å; b = 8.682(4) Å; c = 14.590(8) Å; $\alpha = \gamma$ = 90.0000 °; β = 125.18(2) ° V = 881.00(3) Å^3 R_{wp} = 16.222 %; R_F^2 = 15.800 %						
Atomic Coordinates						
Label	x	y	z	U_{iso} (Å^2)	Fractions	Site
V1	0.1612(9)	0.4781(6)	0.3971(8)	0.0066(8)	1	4e
V2	0.3717(5)	0.4631(9)	0.1174(2)	0.0066(8)	1	4e
P1	0.0317(2)	0.5985(2)	0.1392(5)	0.014(9)	1	4e
P2	0.2575(4)	0.1186(1)	0.1477(2)	0.014(9)	1	4e
P3	0.532(4)	0.2397(5)	0.4976(5)	0.014(9)	1	4e
O1	0.211(8)	0.6096(3)	0.1444(1)	0.016(9)	1	4e
O2	0.0761(8)	0.5002(2)	0.2332(9)	0.016(9)	1	4e
O3	0.1249(7)	0.0387(7)	0.4723(8)	0.016(9)	1	4e
O4	0.0111(6)	0.257(8)	0.3317(4)	0.016(9)	1	4e
O5	0.0921(8)	0.1107(6)	0.1646(3)	0.016(9)	1	4e
O6	0.5989(5)	0.4866(8)	0.2839(9)	0.016(9)	1	4e
O7	0.1889(2)	0.1066(9)	0.0314(3)	0.016(9)	1	4e
O8	0.3690(9)	0.265(5)	0.202(7)	0.016(9)	1	4e
O9	0.3515(7)	0.3263(7)	0.4155(9)	0.016(9)	1	4e
O10	0.5134(7)	0.3634(5)	0.0709(9)	0.016(9)	1	4e
O11	0.699(9)	0.1700(3)	0.0823(8)	0.016(9)	1	4e
O12	0.5683(2)	0.1674(9)	0.4153(2)	0.016(9)	1	4e
Zn1	0.0174(4)	0.787(6)	0.3026(9)	0.00(5)	0.36(5)	4e