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SUPPLEMENTARY INFORMATION

Eco-efficient Splash Combustion Synthesis of Nanoscale Pyrophosphate ($Li_2FeP_2O_7$) Cathodes Using Fe(III) Precursors

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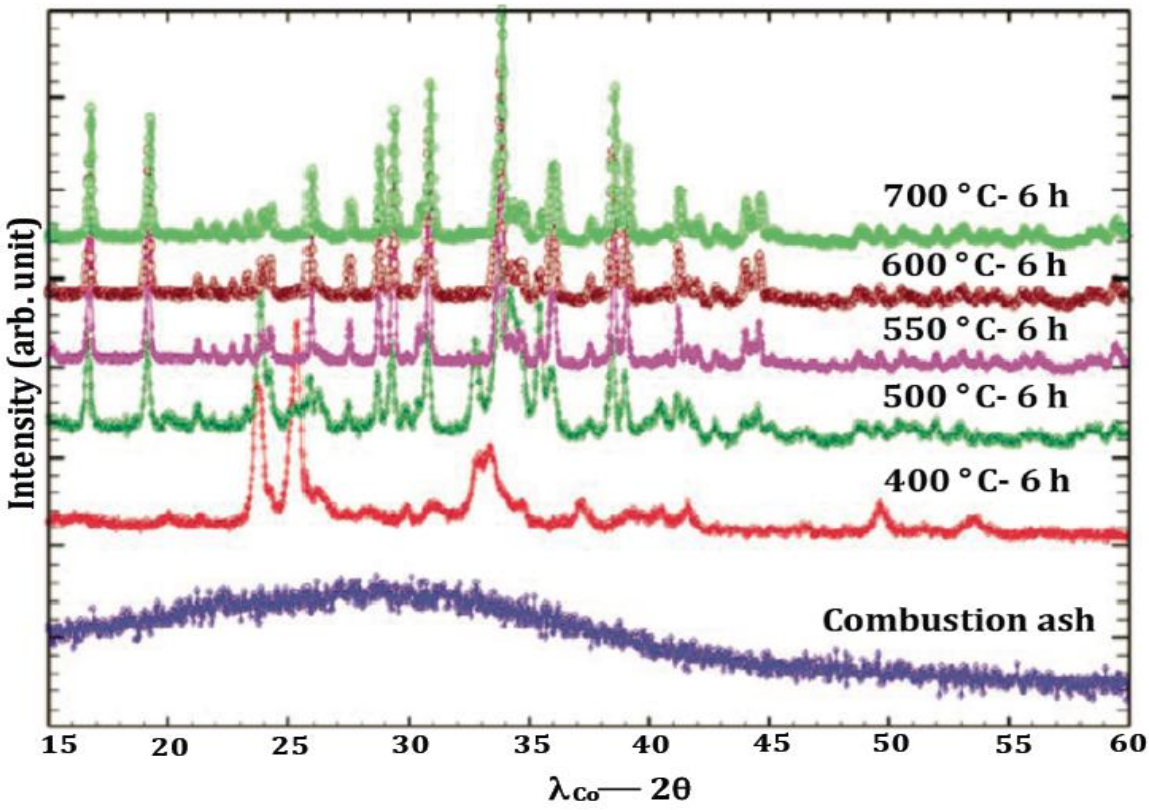

Figure S1: Comparative XRD patterns showing the effect of annealing temperature on the phase evolution of $Li_2FeP_2O_7$. The initial combustion ash shows a broad XRD profile owing to amorphous intermediate complex. High-temperature treatment slowly transforms this complex to form the final product. Single-phase product was obtained at 550°C onwards.

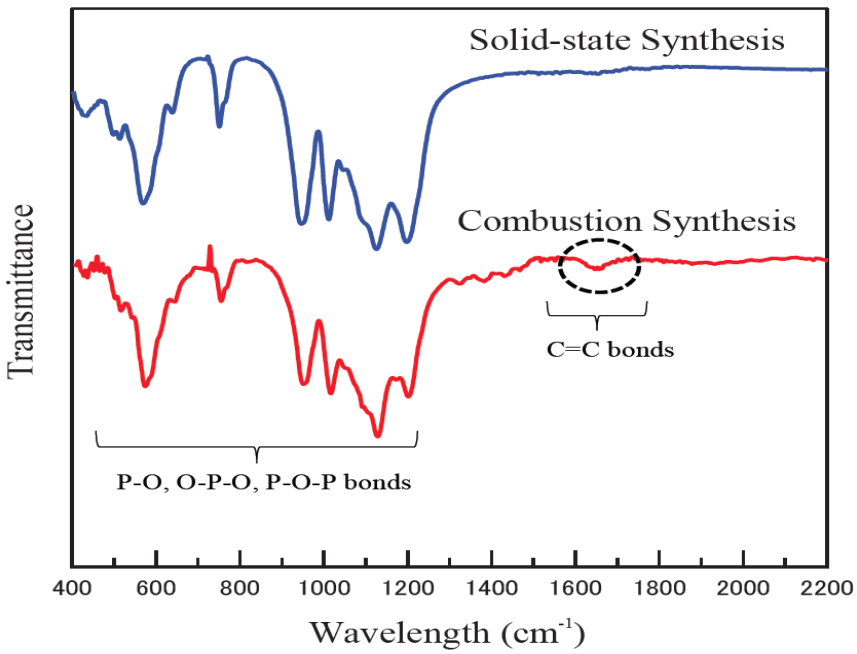

Figure S2: Comparative FT-IR spectra of $Li_2FeP_2O_7$ made by conventional solid-state synthesis and solvothermal (combustion) synthesis. While in P—O—P, O—P—O and P—O bands are common to both sample, the combustion synthesized sample show an extra prominent band at 1600 cm^{-1}, proving the presence of graphitic carbon coating of the pyrophosphate sample.

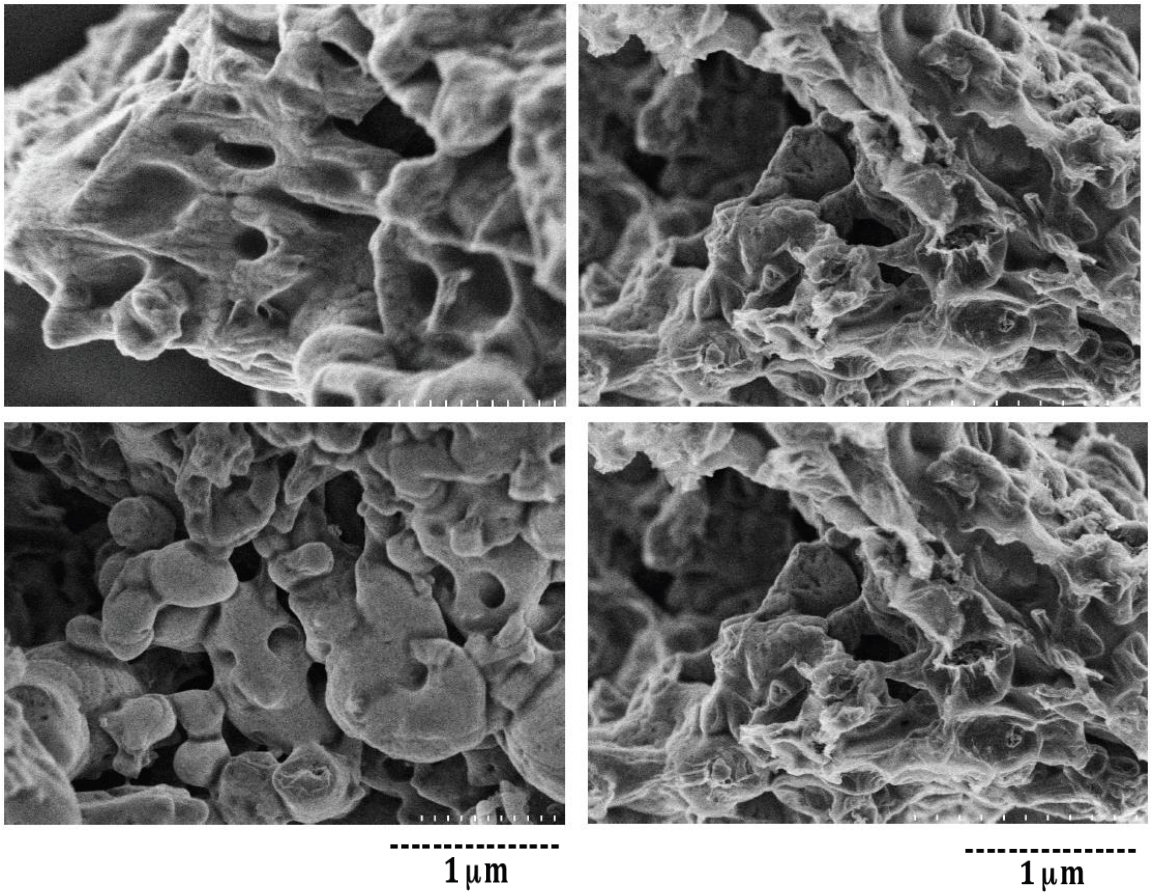

Figure S3: Representative SEM micrographs showing the porous morphology of combustion synthesized $Li_2FeP_2O_7$ particles. The continuous evolution of gaseous products leads to this porous morphology.

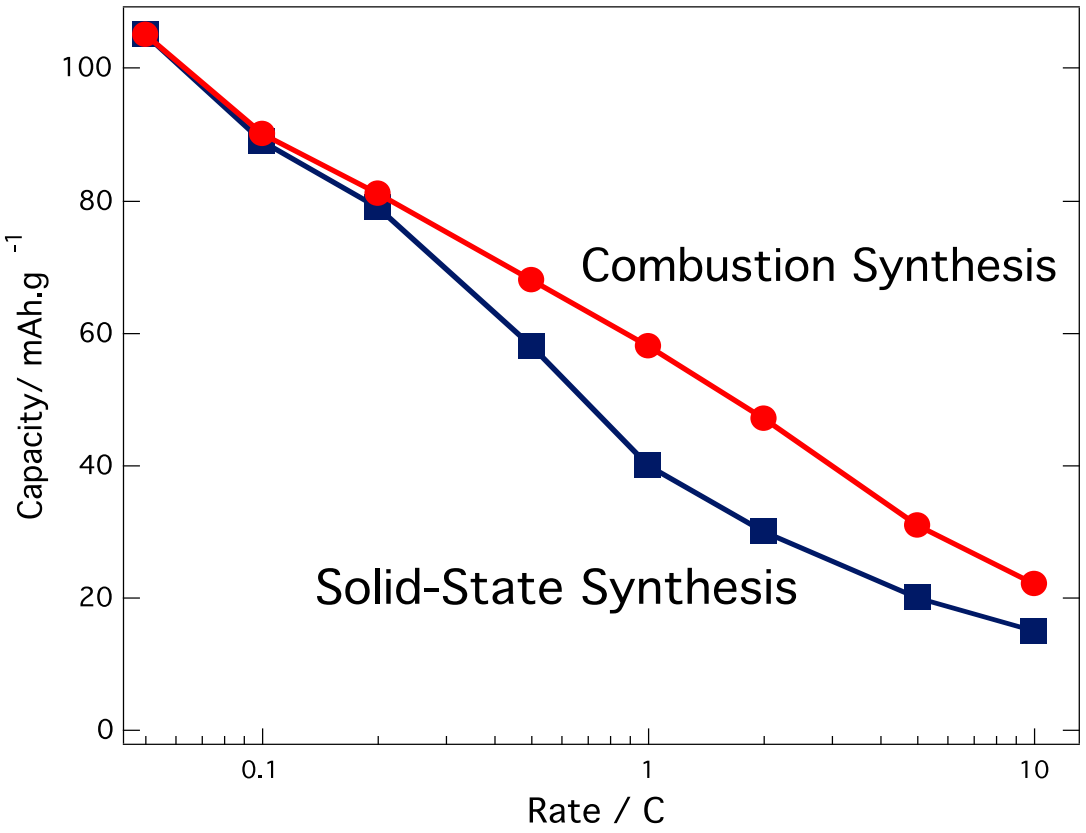

Figure S4: Power rate capability of splash combustion synthesized $Li_2FeP_2O_7$ vs solid-state synthesized $Li_2FeP_2O_7$. Though combustion synthesized (nanometric) product gives slightly better capacity at faster rate, the overall capacity is quite independent of particle size owing to its two-dimensional diffusion channels.

Table 1: Lattice parameters of combustion synthesized $Li_2(Fe_{1-x}Mn_x)P_2O_7$ phases assuming the monoclinic structure (s.g. $P2_1/c$). In all cases, the χ^2 values were less than 3.5.

Materials	a (Å)	b (Å)	c (Å)	β (°)	Vol (Å^3)
$Li_2FeP_2O_7$	11.0051(3)	9.7474(4)	9.8008(3)	101.50(3)	1030.217(4)
$Li_2(Fe_{0.8}Mn_{0.2})P_2O_7$	11.0637(5)	9.7771(5)	9.8433(4)	101.83(5)	1042.139(2)
$Li_2(Fe_{0.5}Mn_{0.5})P_2O_7$	11.1008(2)	9.8063(7)	9.8776(6)	101.97(6)	1051.962(2)
$Li_2(Fe_{0.2}Mn_{0.8})P_2O_7$	11.1058(4)	9.8633(2)	9.8895(8)	102.05(5)	1060.111(3)
$Li_2MnP_2O_7$	11.1118(6)	9.9173(8)	9.9074(7)	102.21(7)	1066.978(6)

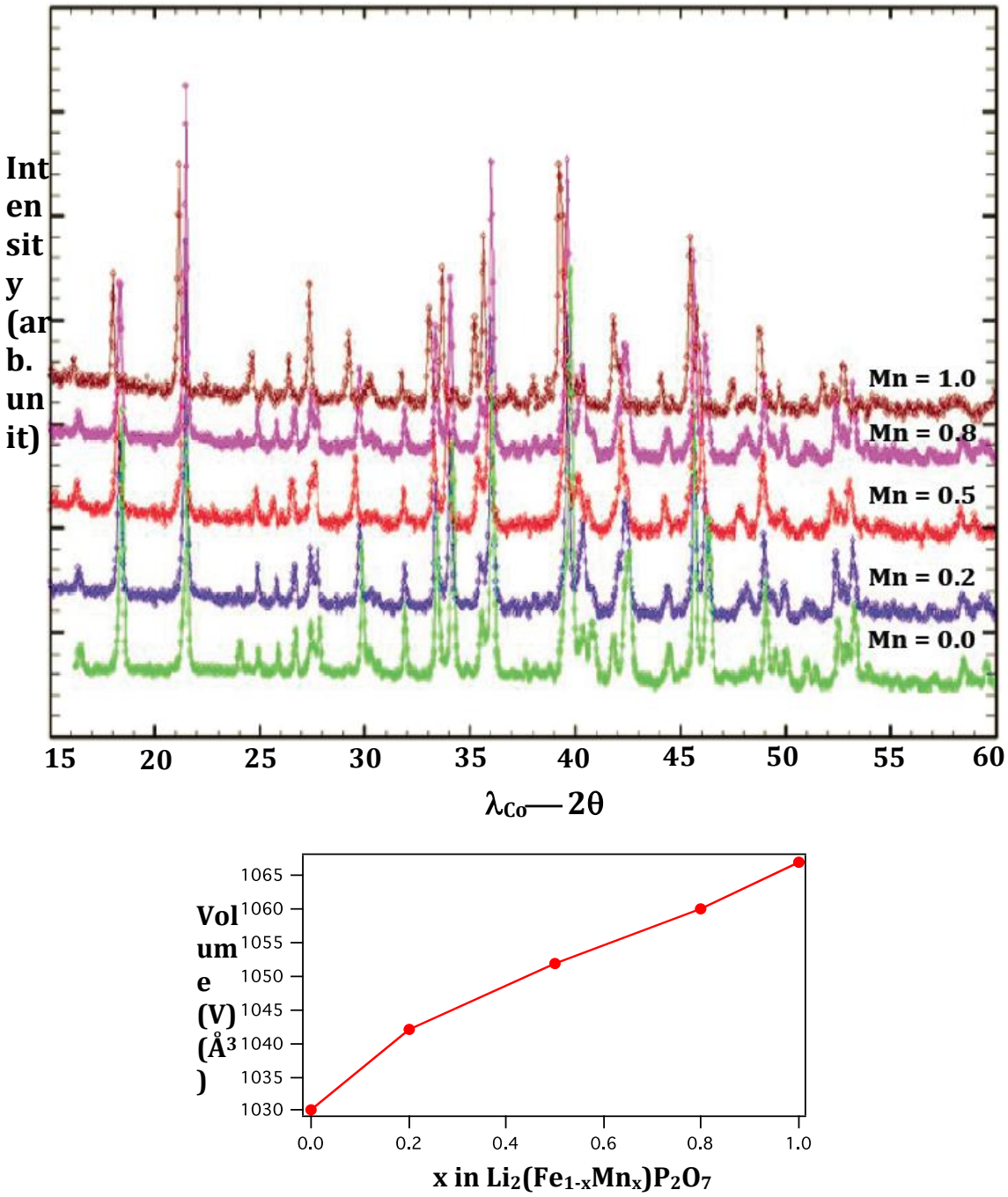

Figure S5: *(Top)* X-ray powder diffraction patterns of combustion synthesized mixed metal pyrophosphates, $Li_2(Fe_{1-x}Mn_x)P_2O_7$ (x = 0, 0.2, 0.5, 0.8 and 1), produced at 600 °C (6 h). A complete solid-solution series can be easily obtained showing the versatility of the combustion route. Higher Mn content moves the XRD peaks to lower diffraction angle owing to larger ionic size of Mn (higher lattice constants). (*Bottom*) The lattice parameters and volume gradually increases with Mn content.

General notes about the combustion synthesis of $LiFePO_4$.—

Similar to $Li_2FeP_2O_7$, combustion synthesis process can be easily applied to $LiMPO_4$ (M = Fe/Mn/Co) olivine system, by using Fe(III) based economic precursors. In fact, combustion synthesis can produce single-phase olivine products at low temperature of 300 °C, whereas conventional solid-state synthesis requires at least 500 °C. So, temperature can be reduced by at least 200 °C. Also, using combustion synthesis, the product can be formed within 1 hour.

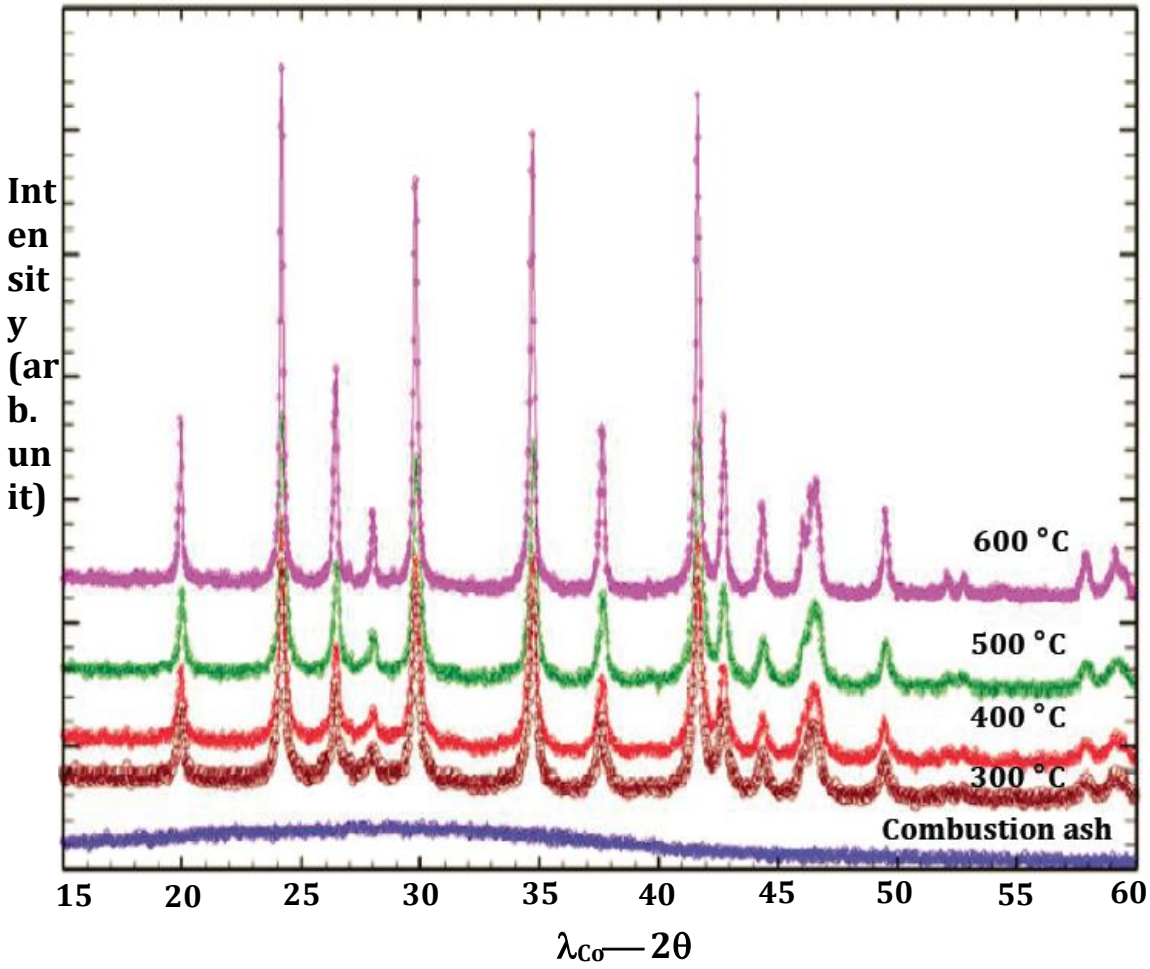

Figure S6: Comparative XRD patterns of combustion synthesized $LiFePO_4$ annealed at different temperature. The initial combustion ash shows a broad XRD profile indicating the presence of an amorphous intermediate complex. High-temperature treatment slowly transforms this complex to form the final product. Single-phase $LiFePO_4$ was obtained at a low temperature of 300 °C. The broad XRD peaks show the formation of very small particles. Higher annealing temperature leads to larger particles and hence sharper XRD peaks.

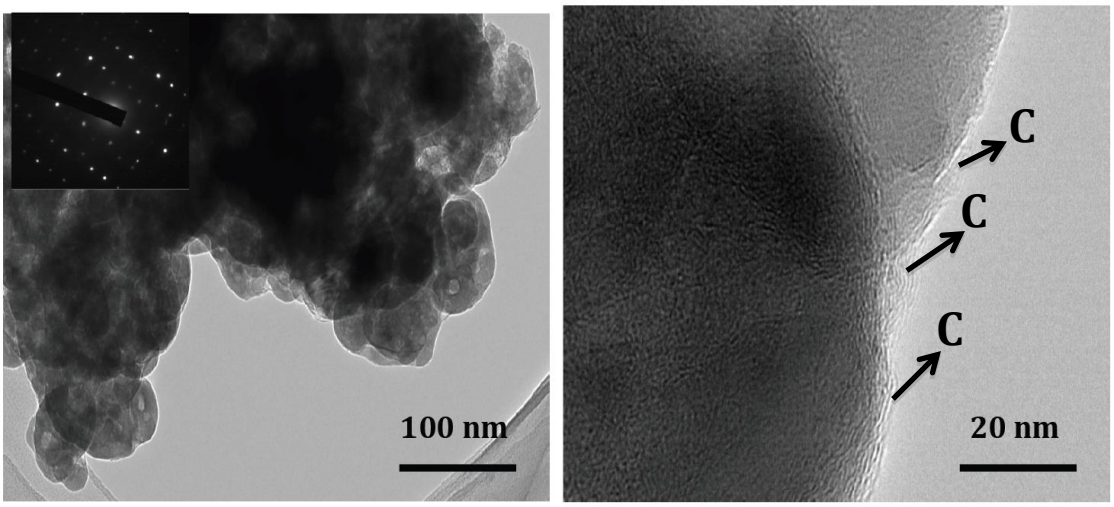

Figure S7: *(Left)* HRTEM images of combustion synthesized $LiFePO_4$ showing fine particles below 100 nm. (*Right*) TEM observation of the formation of a thin (3-5 nm) layer of carbon coating on the individual $LiFePO_4$ particles (as pointed by arrow marks). Thus, combustion synthesis can facilitate both 'nano-sizing' and 'carbon coating', two essential points to develop electroactive olivine cathode.

Table 2: Lattice parameters of combustion synthesized $Li(Fe_{1-x}Mn_x)PO_4$ powders, assuming the orthorhombic structure (s.g. *Pnma*). In all cases, the χ^2 values were less than 2.

Materials	a (Å)	b (Å)	c (Å)	Vol (Å^3)
$LiFePO_4$	10.3313(3)	6.0077(1)	4.6911(3)	291.112(1)
$Li(Fe_{0.8}Mn_{0.2})PO_4$	10.3651(6)	6.0293(3)	4.7127(2)	294.527(1)
$Li(Fe_{0.5}Mn_{0.5})PO_4$	10.4183(2)	6.0732(8)	4.7466(5)	300.334(3)
$Li(Fe_{0.2}Mn_{0.8})PO_4$	10.4588(4)	6.1084(4)	4.7621(5)	304.238(7)
$LiMnPO_4$	10.4772(2)	6.1247(4)	4.7677(5)	305.951(4)

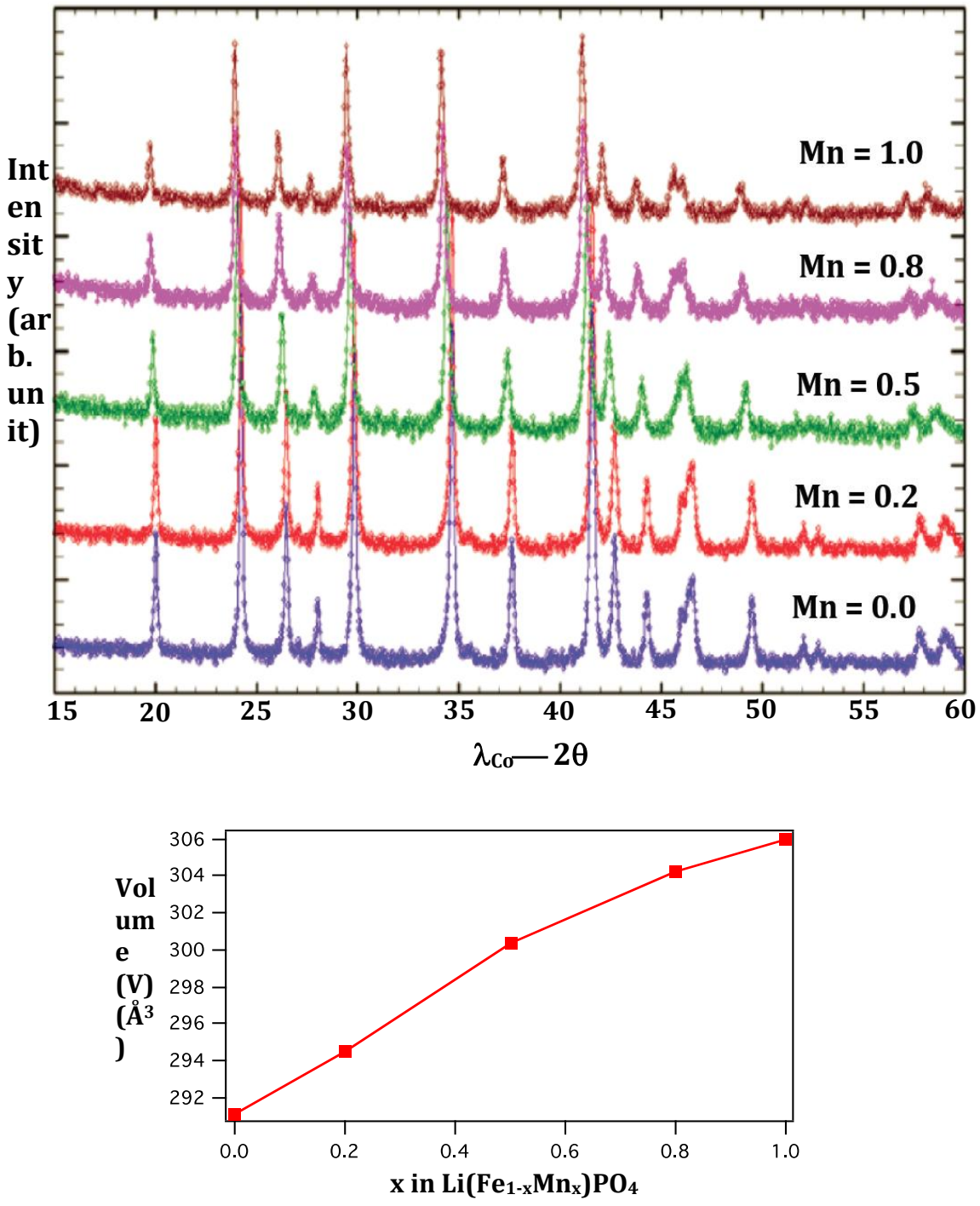

Figure S8: *(Top)* Combustion synthesized mixed-metal $Li(Fe_{1-x}Mn_x)PO_4$ olivine (x = 0, 0.2, 0.5, 0.8 and 1), showing gradual up shift in the XRD peaks with higher Mn-content owing to its larger ionic radii. These phases were produced at 300 °C for 1h. (*Bottom*) The gradual increase in lattice volume with Mn content is shown.