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Understanding the stability of $MnPO_4$

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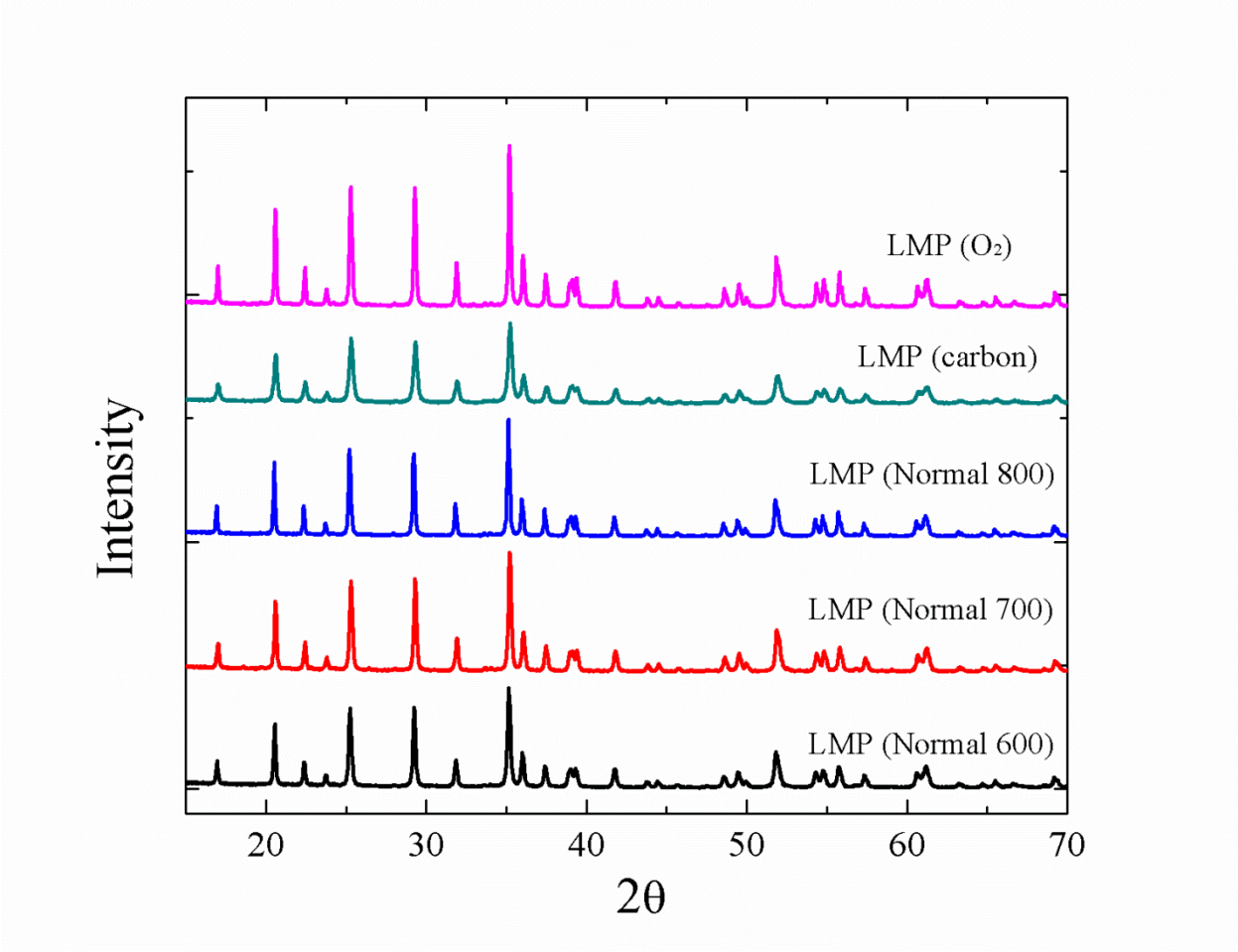

Fig S1: XRD patterns of $LiMnPO_4$ series.

Table S1: Lattice parameters of $LiMnPO_4$ series.

$LiMnPO_4$	a (Å)	b (Å)	c (Å)	Volume (Å)	R_p
LMP-RC-600	10.460(1)	6.111(1)	4.750(1)	303.6	6.85
LMP-RC-700	10.457(1)	6.109(1)	4.748(1)	303.3	6.71
LMP-RC-800	10.452(1)	6.107(1)	4.747(1)	303.0	7.98
LMP-CC-700	10.448(1)	6.105(1)	4.748(1)	302.8	6.46
LMP-NC-700	10.448(1)	6.104(1)	4.745(1)	302.6	6.96

Table S2: Elemental analysis and ICP results of $LiMnPO_4$ series.

Sample	Color	Carbon, wt.%	H, wt.%	ICP ratio Li:Mn:P
LMP-RC-600	Grey	0.34	0	1.00:1.03:1
LMP-RC-700	Grey	0.33	0	1.03:1.04:1
LMP-RC-800	Grey	0.23	0	1.04:1.04:1
LMP-CC-700	Black	2.02	0	1.00:1.04:1
LMP-NC-700	White	0	0	1.00:1.03:1

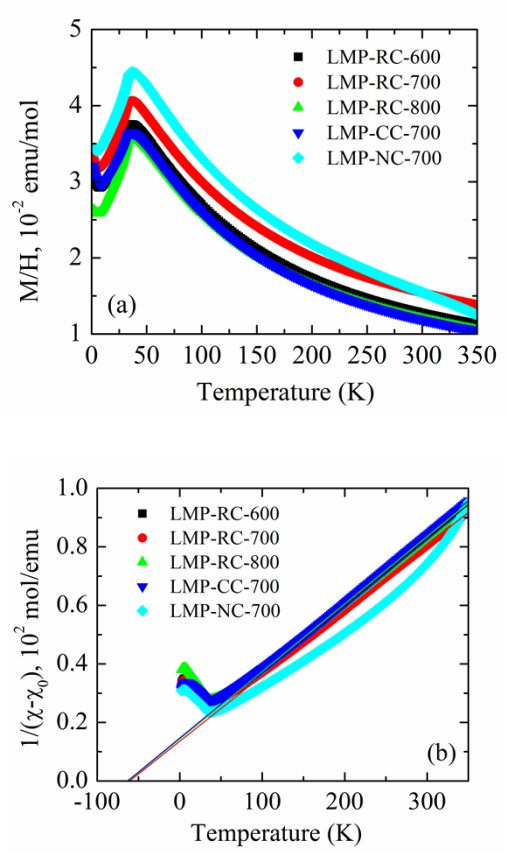

Fig S2: (a) Temperature dependence of the magnetic susceptibility of $LiMnPO_4$ series and (b) inverse susceptibilities corrected for temperature-independent contribution and their fit to the Curie-Weiss law.

Table S3: Magnetic parameters of $LiMnPO_4$ series.

$LiMnPO_4$	Θ (K)	C (emu·K/mol)	μ (μ_B)	χ_0 (emu/mol)	T_N (K)
LMP-RC-600	-63.2	4.375	5.92	$7.4 \cdot 10^{-4}$	33
LMP-RC-700	-60.6	4.473	5.98	$3.0 \cdot 10^{-3}$	33
LMP-RC-800	-62.4	4.338	5.89	0	33
LMP-CC-700	-63.2	4.315	5.88	0	32.5
LMP-NC-700	-	-	-	$2 \cdot 10^{-3}$	33

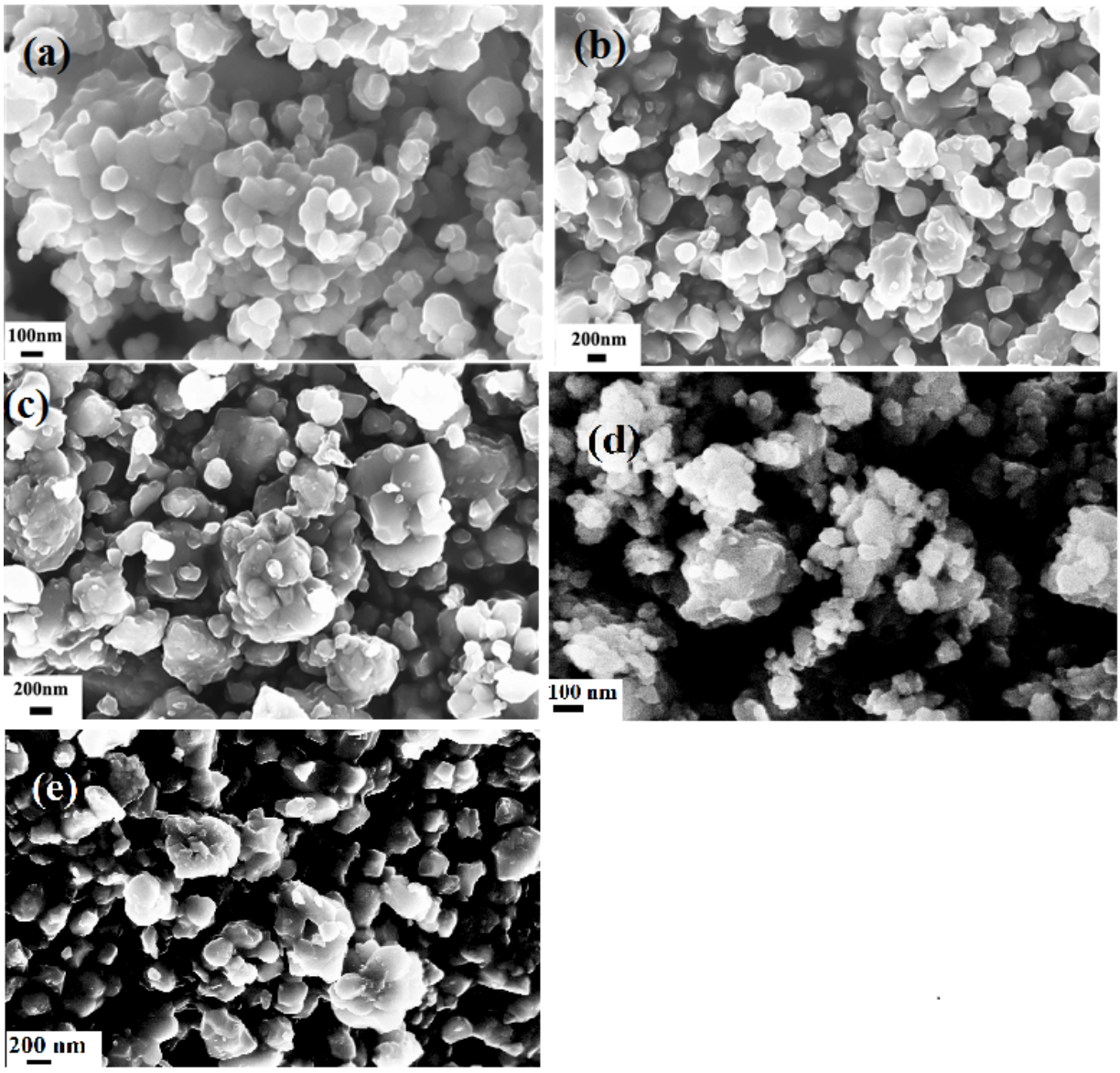

Fig S3: SEM images of (a) LMP-RC-600, (b) LMP-RC-700, (c) LMP-RC-800, (d) LMP-CC-700 and (e) LMP-NC-700.

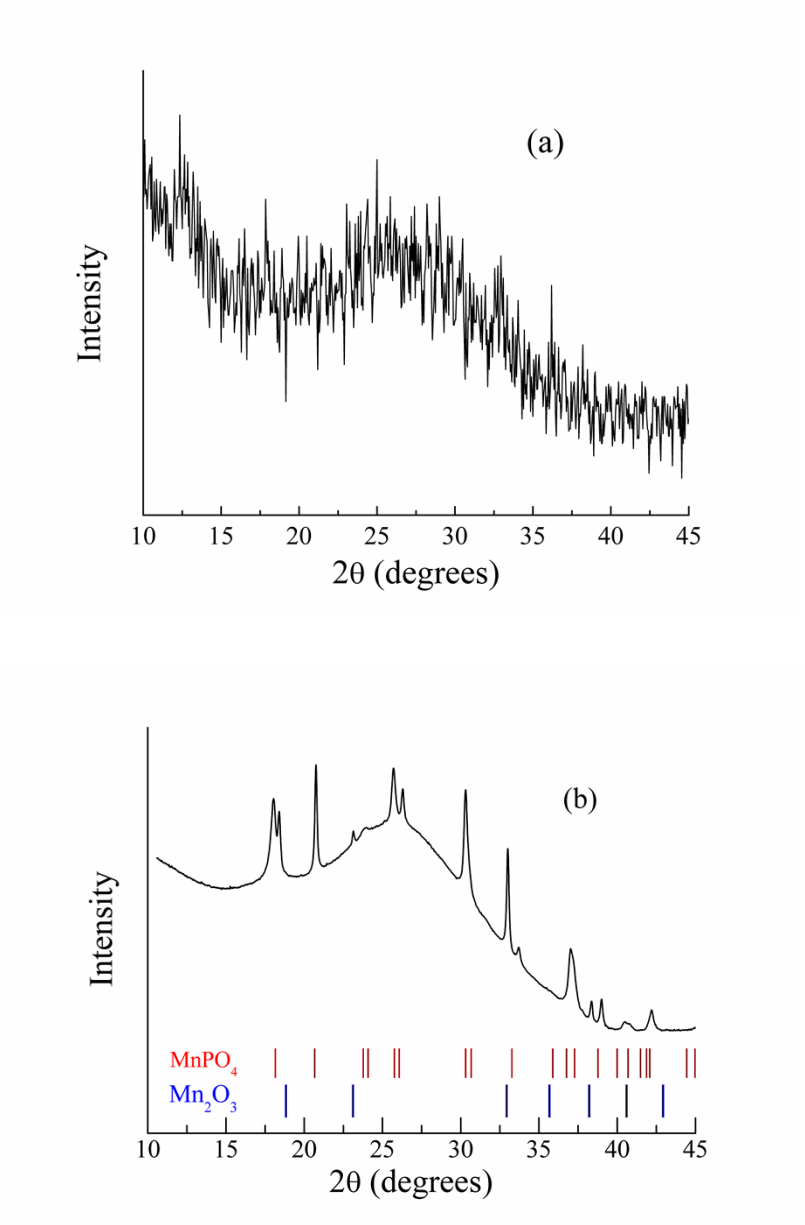

Fig S4: (a) X-ray diffraction pattern of MP-NC-700 λ=1.54 Å, (b) synchrotron X-ray diffraction pattern of MP-NC-700 converted to λ=1.54 Å.

Using Cu Kα, we can hardly see any peak in XRD patterns. But in synchrotron X-ray, some small peaks can be observed, suggesting that the amorphous compound MIGHT consist of $MnPO_4$ and Mn_2O_3 (PDF 04-005-4361).

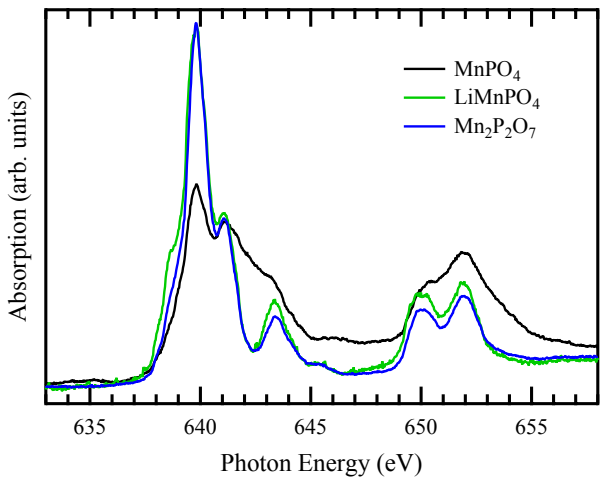

Figure S5: Mn $L_{3,2}$-edge XAS of $MnPO_4$, $LiMnPO_4$, and $Mn_2P_2O_7$ powders as measured in TEY mode.

Complimentary Mn $L_{3,2}$-edge X-ray absorption spectroscopy measurements were performed at the undulator beamline X1B at the NSLS using the Boston University endstation. The XAS spectra were recorded in both total electron yield (TEY) and total fluorescent yield (TFY) modes with an effective beamline resolution of 0.2 meV. The absorption spectra were normalized to the current from a reference Au-coated mesh in the incident photon beam. The energy scale of the XAS measurements was calibrated using first- and second- order diffraction Ti $L_{3,2}$-edge absorption features of rutile TiO_2. The XA spectra of the $LiMnPO_4$ and $Mn_2P_2O_7$ are consistent with spectral line shapes of Mn^{2+}, whereas $MnPO_4$ displays a line shape indicating Mn^{3+} in agreement with the literature.[1,2] This reaffirms our assignments of Mn oxidation states in our XPS analysis.

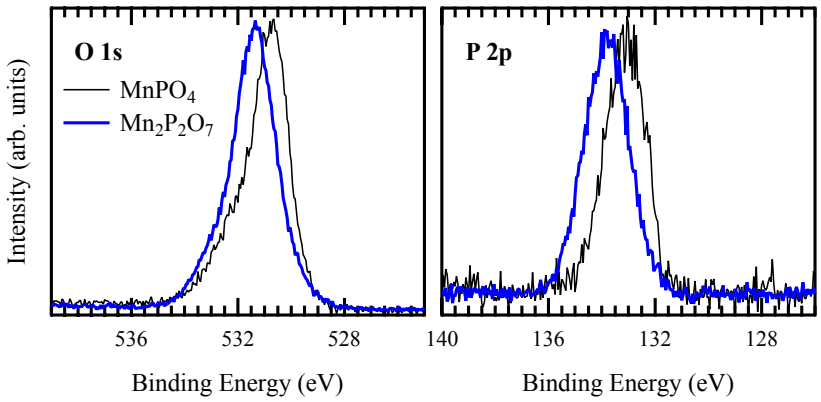

Figure S6: O1s and P 2p core level XPS.

We observe a difference in binding energy of ~0.8 eV between the $MnPO_4$ and $Mn_2P_2O_7$ in both the O1s and P 2p core level peaks.

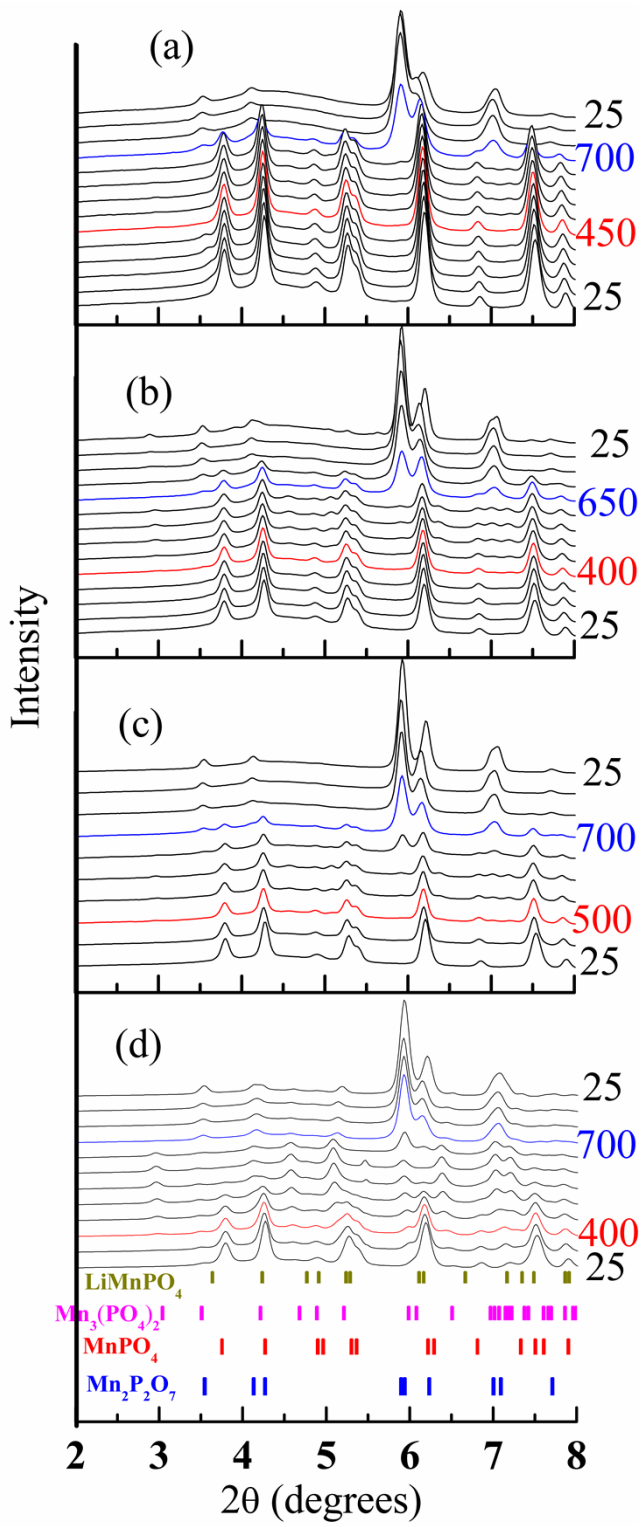

Fig. S7: X-ray diffraction patterns upon heating of MP samples in O_2. $\lambda = 0.3196$Å. Red curves give the temperature where sarcopside $Mn_3(PO_4)_2$ starts to form. Blue curves show the final decomposition temperature.

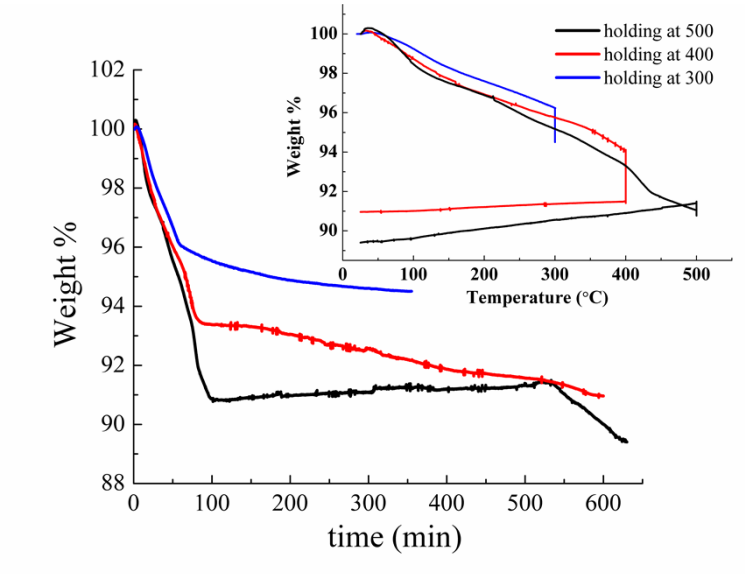

Fig. S8: TGA curves of $MnPO_4$ holding at 300, 400 and 500 °C for over 5 hours in ambient atmosphere.

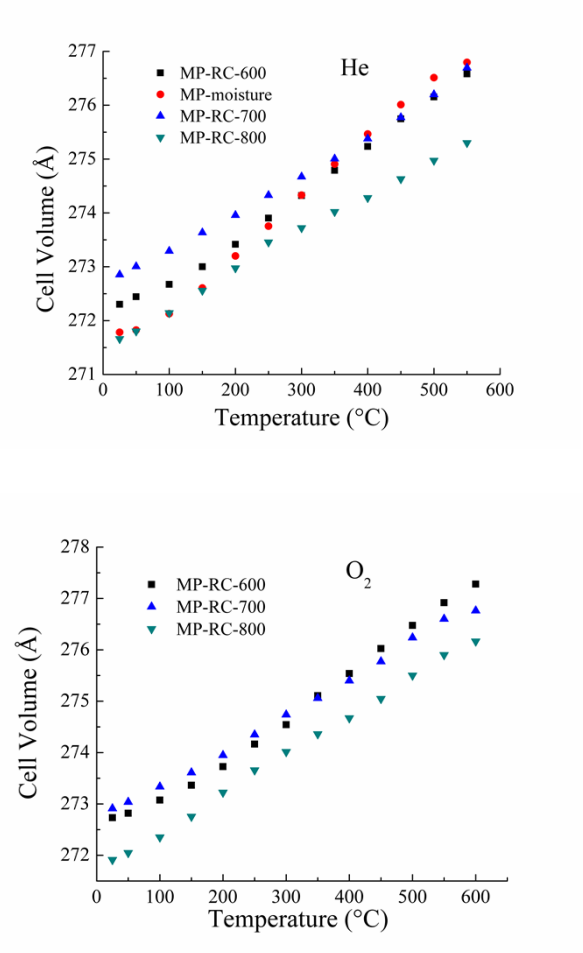

Fig. S9: Unit cell volumes as a function of temperature of $MnPO_4$ series in (top) N_2 and (bottom) O_2 atmospheres.

References:

1. L. F. J. Piper, N. F. Quackenbush, S. Sallis, D. O. Scanlon, G. W. Watson, K.-W. Nam, X.-Q. Yang, K. E. Smith, F. Omenya, N. A. Chernova, M. S. Whittingham, *J. Phys. Chem. C* 2013, **117**, 10383–10396.
2. L. F. J. Piper, A. R. H. Preston, S. W. Cho, A. DeMasi, B. Chen, J. Laverock, K. E., Smith, L. J. Miara, J. N. Davis, S. N. Basu, U. Pal, S. Gopalan, L. Saraf, T. Kaspar, A. Y., Matsuura, P. A. Glans and J. H. Guo. *J. Electrochem. Soc.*, 2011, **158**, B99.