Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

PO_4^{3-} polyanion-doping for stabilizing Li-rich layered oxides as cathode for advanced lithium-ion batteries

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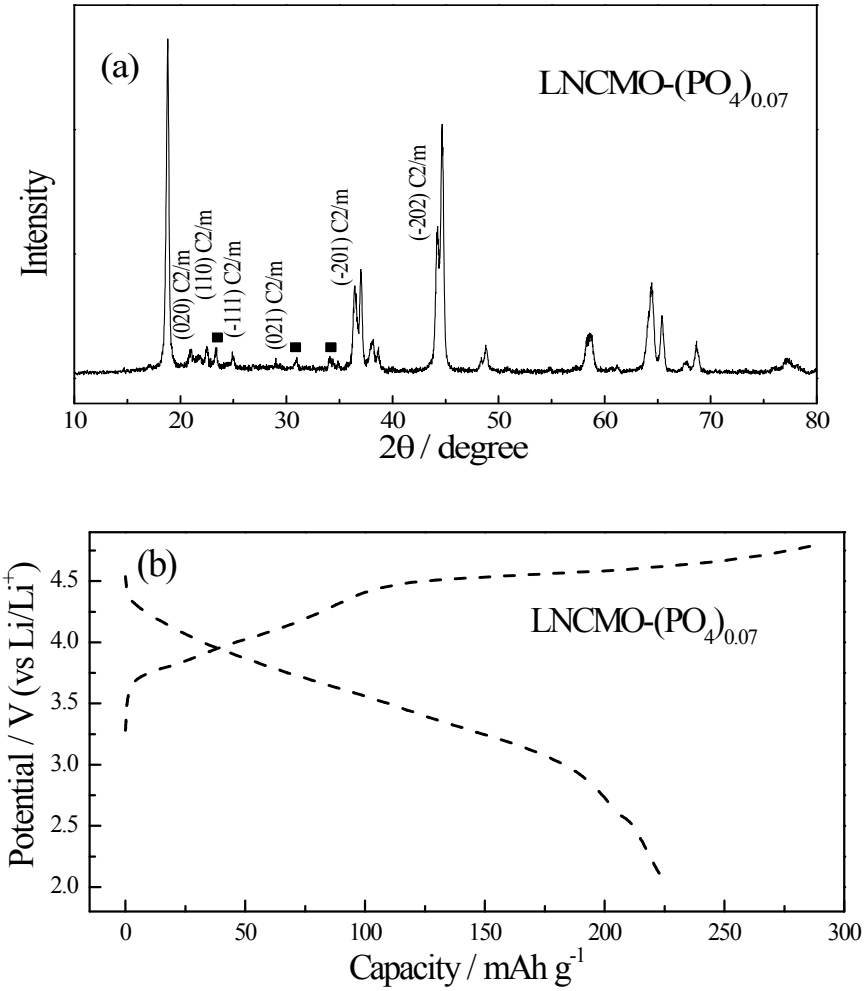
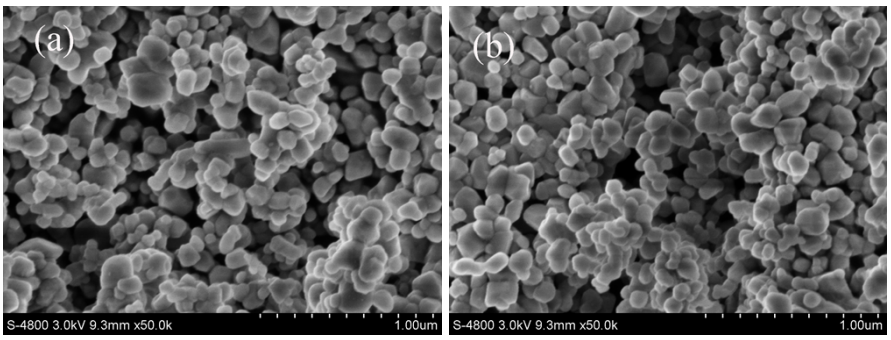


Fig. S1. (a) XRD patterns and (b) initial charge/discharge curves of the LNCMO-$(PO_4^{3-})_{0.07}$ oxide.



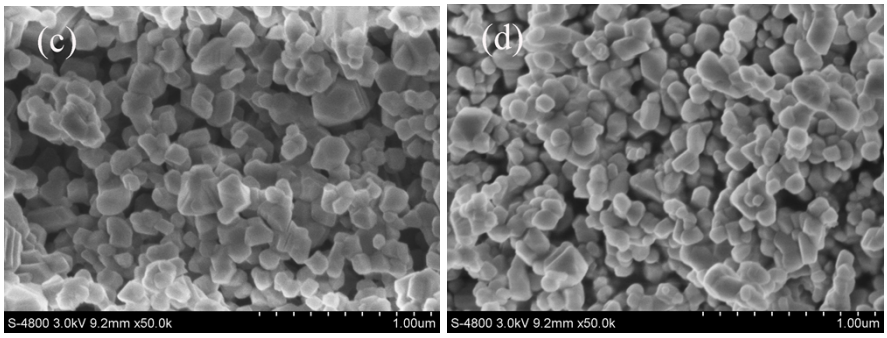


Fig. S2. SEM images of the oxides. (a) LNCMO, (b) LNCMO-$(PO_4)_{0.01}$ (c) LNCMO-$(PO_4)_{0.03}$ and (d) LNCMO-$(PO_4)_{0.05}$.

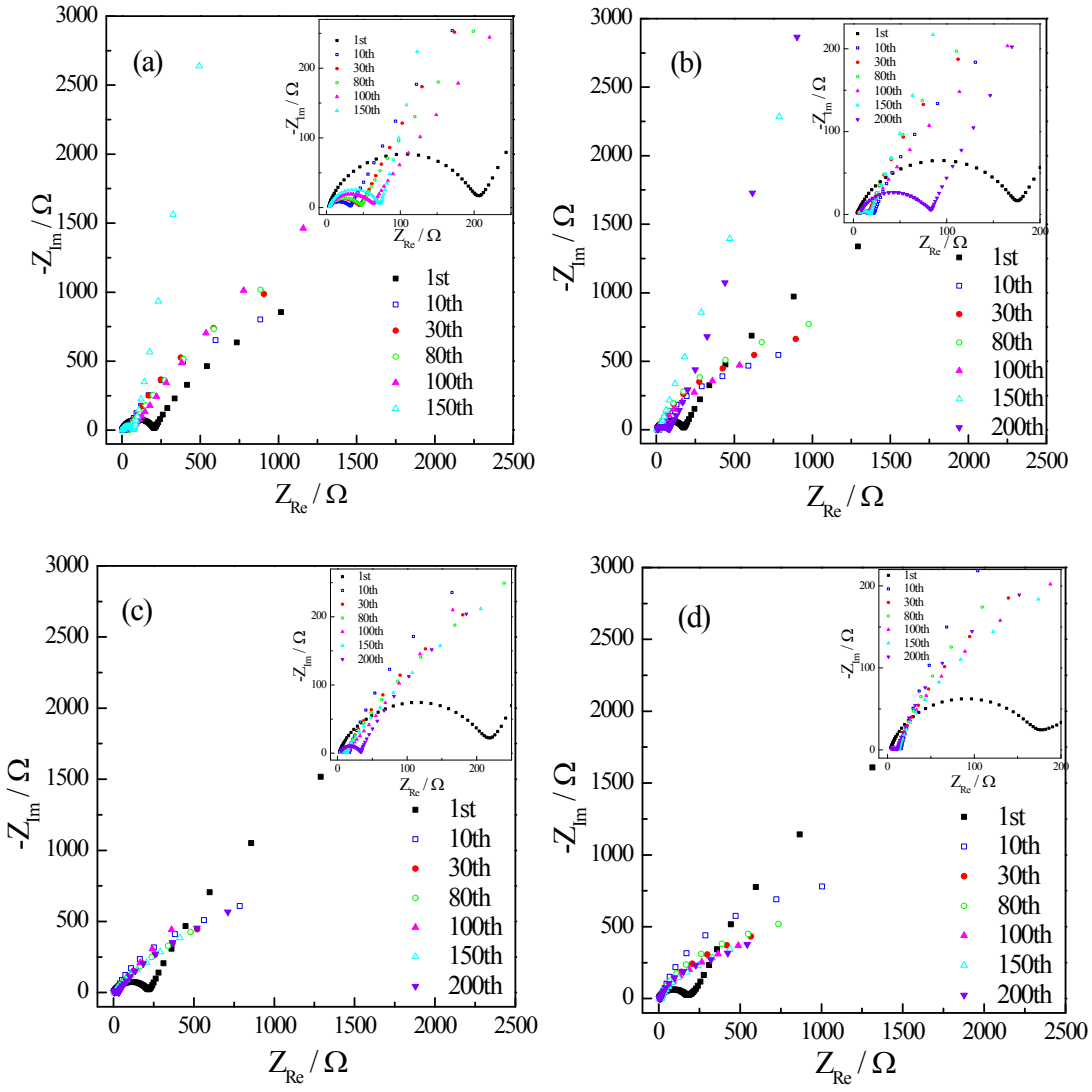


Fig. S3. Electrochemical impedance spectra (EIS) of the oxides in different cycles at 0.1C rate (30 mA g^{-1}). (a) LNCMO, (b) LNCMO-$(PO_4)_{0.01}$ (c) LNCMO-$(PO_4)_{0.03}$ and (d) LNCMO-$(PO_4)_{0.05}$. The insets are enlarged spectra in the high frequency region. EIS were measured in the open-circuit mode when discharged to 2.0V (vs Li/Li^+).

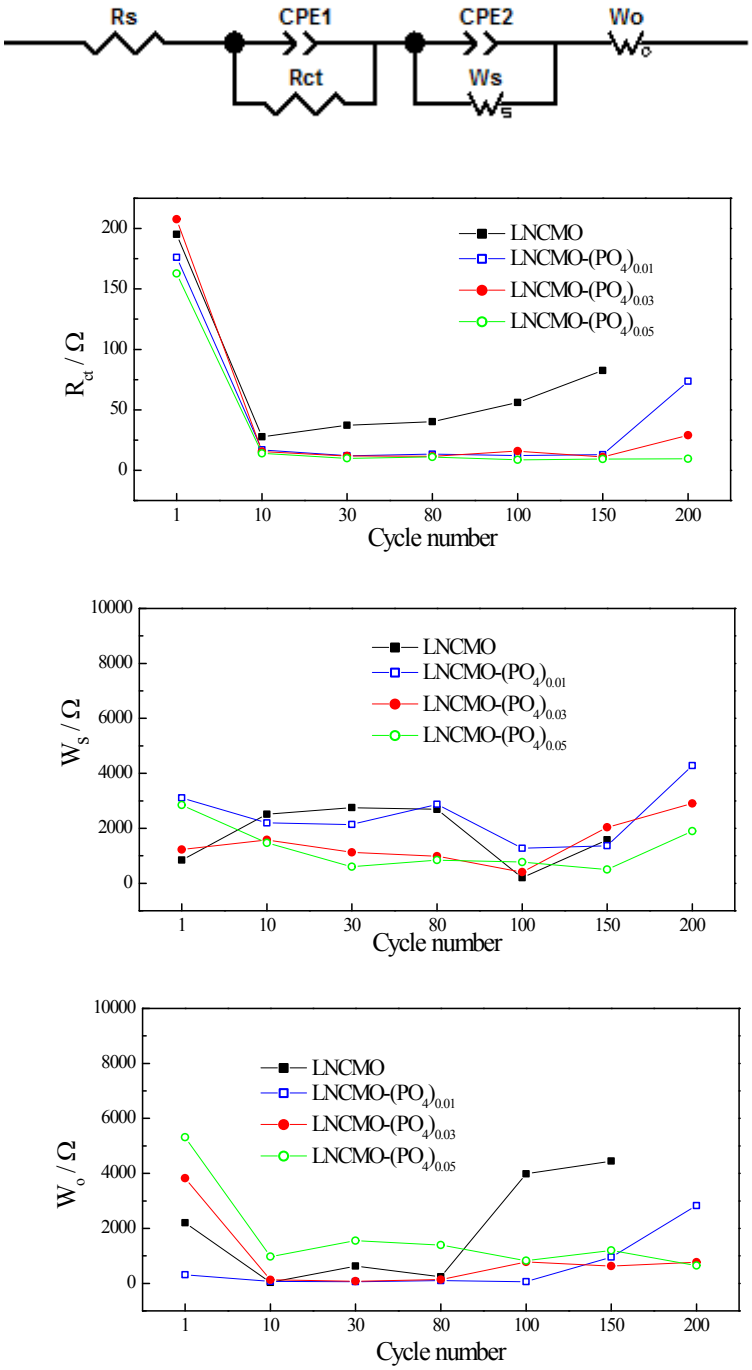


Fig. S4. Equivalent circuits used to fit the experimental data. R_s is solution resistance, R_{ct} is charge-transfer resistance, CPE and CPE1 are constant phase element, W_s and W_o are assigned to the finite Nernst diffusion impedance in the thin film and semi-infinite Warburg diffusion impedance in the bulk, respectively. The simulated R_{ct}, W_s and W_o values with different cycles are presented.

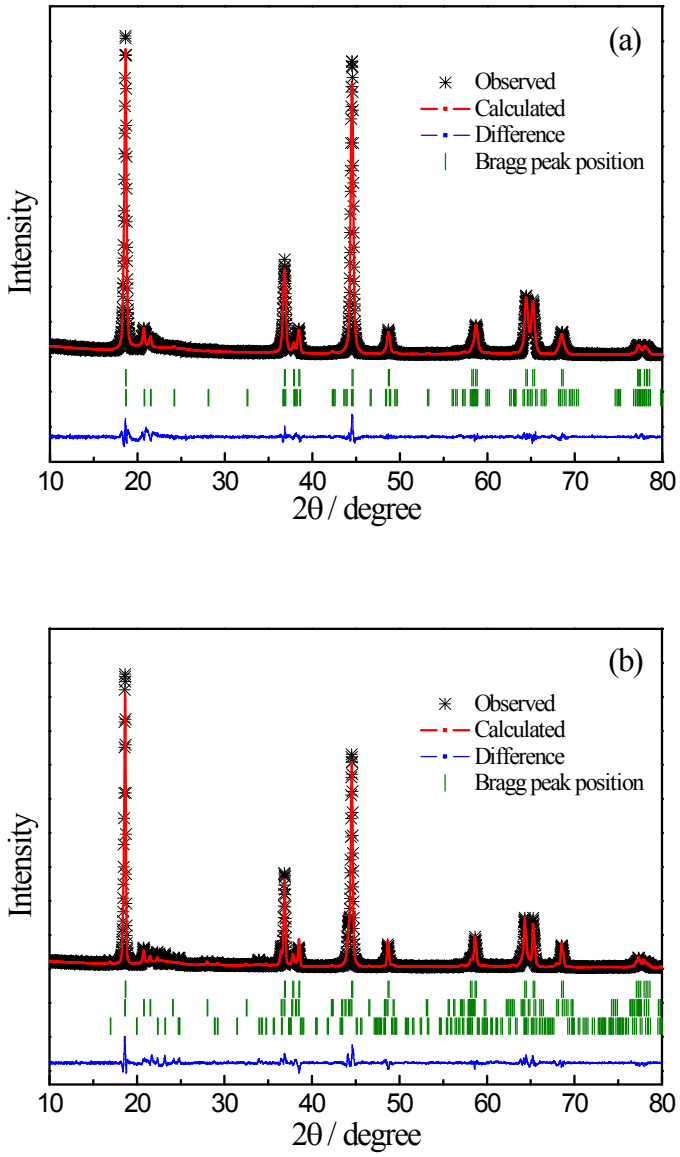


Fig. S5. Reitveld refinements of the pristine LNCMO (a) and LNCMO-$(PO_4)_{0.05}$ (b) based on the $LiNi_{0.4}Co_{0.1}Mn_{0.5}O_2$ ($R\bar{3}m$) and Li_2MnO_3 (C2/m) structure.($Li_{1.17}Ni_{0.20}Mn_{0.58}Co_{0.05}O_2$ can be considered as 5/6 ($0.4Li_2MnO_3 \cdot 0.6LiNi_{0.4}Co_{0.1}Mn_{0.5}O_2$)). Li_3PO_4 as a trace of impurity is also introduced in the structure refinement of LNCMO-$(PO_4)_{0.05}$.

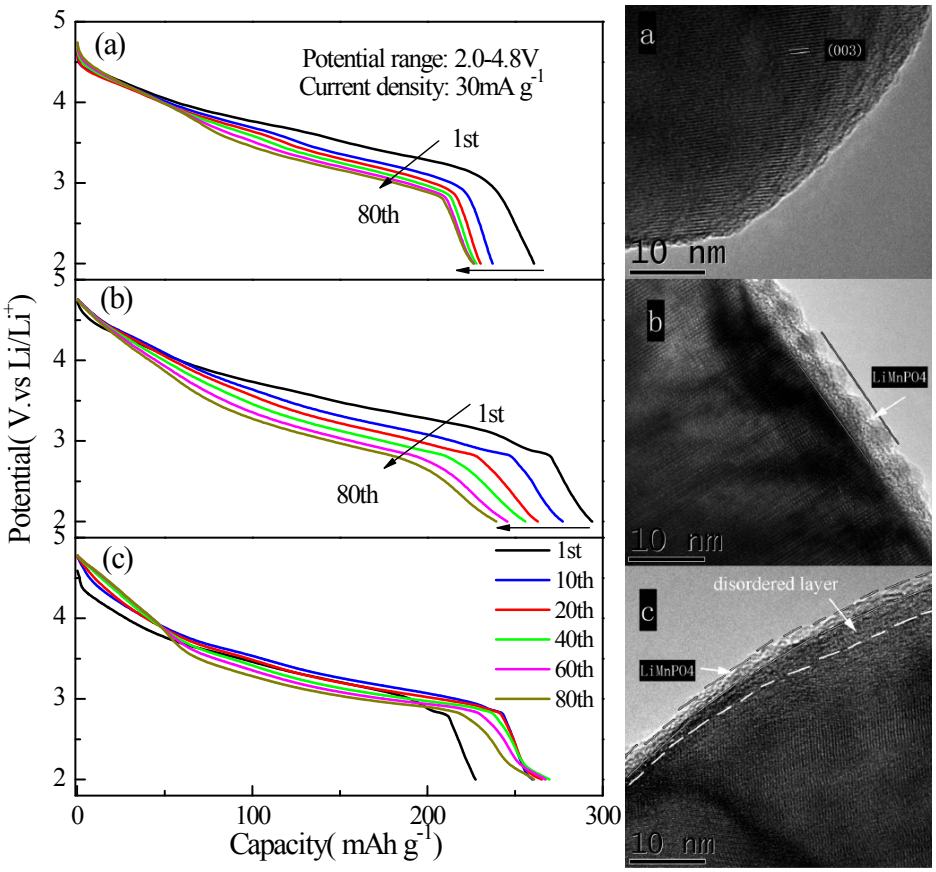
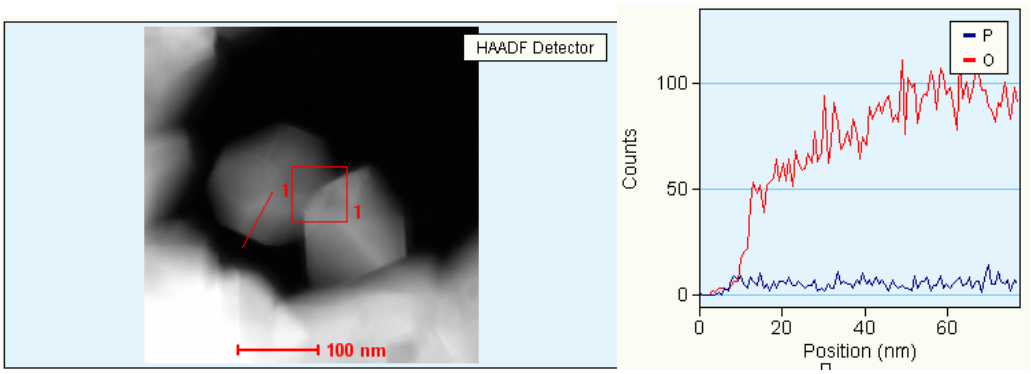


Fig. S6. The discharge curves of the as-prepared $Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ (a) and Li-Mn-PO_4 (5wt %) coated samples after calcination at 400 °C (b) and 500 °C (c) at different cycles. Reproduced with permission.[1] Copyright 2013, Royal Society of Chemistry.



(a) (b)

Fig. S7. HAADF-STEM image (a) and corresponding line-scanning (b) of oxygen and phosphor elements across a selected area (red line 1 in a) of the LNCMO-$(PO_4)_{0.05}$ oxide.

Table S1. The atom parameters of $LiNi_{0.4}Co_{0.1}Mn_{0.5}O_2$ phase in LNCMO and LNCMO-$(PO_4)_{0.05}$ materials. sg = space group, occ = site occupancy. $Li_{1.17}Ni_{0.20}Mn_{0.58}Co_{0.05}O_2$ can be considered as 5/6 ($0.4Li_2MnO_3 \cdot 0.6LiNi_{0.4}Co_{0.1}Mn_{0.5}O_2$)

sg:$R\bar{3}m$	LNCMO				LNCMO-$(PO_4)_{005}$			
	x	y	z	occ	x	y	z	occ
Li (3a)	0	0	0	0.85543	0	0	0	0.98812
Li (3b)	0	0	0.5	0.14457	0	0	0.5	0.01188
Ni (3a)	0	0	0	0.14457	0	0	0	0.01188
Ni (3b)	0	0	0.5	0.26343	0	0	0.5	0.39612
Co (3b)	0	0	0.5	0.10200	0	0	0.5	0.10200
Mn (3b)	0	0	0.5	0.49000	0	0	0.5	0.49000
O (6c)	0	0	0.24892	1	0	0	0.24892	1

Table S2. The atom parameters of Li_2MnO_3 phase in LNCMO and LNCMO-$(PO_4)_{0.05}$ materials. sg = space group, occ = site occupancy. $Li_{1.17}Ni_{0.20}Mn_{0.58}Co_{0.05}O_2$ can be considered as $5/6(0.4Li_2MnO_3 \cdot 0.6LiNi_{0.4}Co_{0.1}Mn_{0.5}O_2)$.

sg: C2/m	LNCMO				LNCMO-$(PO_4)_{005}$			
	x	y	z	occ	x	y	z	occ
Li (2b)	0	0.5	0	0.53158	0	0.5	0	0.7028
Li (2c)	0	0	0.5	0.96834	0	0	0.5	0.81338
Li (4h)	0	0.74961	0.5	0.91919	0	0.67250	0.5	0.79645
Li (4g)	0	0.17767	0	0.34506	0	0.19406	0	0.44546
Mn (2b)	0	0.5	0	0.46842	0	0.5	0	0.2972
Mn (2c)	0	0	0.5	0.03166	0	0	0.5	0.18662
Mn (4h)	0	0.74961	0.5	0.08081	0	0.67250	0.5	0.20355
Mn (4g)	0	0.17767	0	0.65494	0	0.19406	0	0.55454
O (4i)	0.20956	0	0.19784	1	0.13283	0	0.17804	1
O (8j)	0.26657	0.32060	0.22571	1	0.20433	0.32707	0.21810	1

Table S3. Summary of R factors and crystallographic parameters for LNCMO and LNCMO-$(PO_4)_{0.05}$.

	Rwp (%)	Rp (%)	Cell parameters (Å)			Ni in Li layer (%)
			a	b	c	
LNCMO	15.7	13.6	2.8585	2.8585	14.2415	14.4%
LNCMO-$(PO_4)_{005}$	19.3%	22.1%	2.8588	2.8588	14.2835	1.2%

References

[1] Q. Q. Qiao, H. Z. Zhang, G. R. Li, S. H. Ye, C. W. Wang, X. P. Gao, *J. Mater. Chem*. A, **2013**, 1, 5262.