Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information

Enhancing the electrochemical kinetics of high voltage olivine $LiMnPO_4$ by isovalent co-doping

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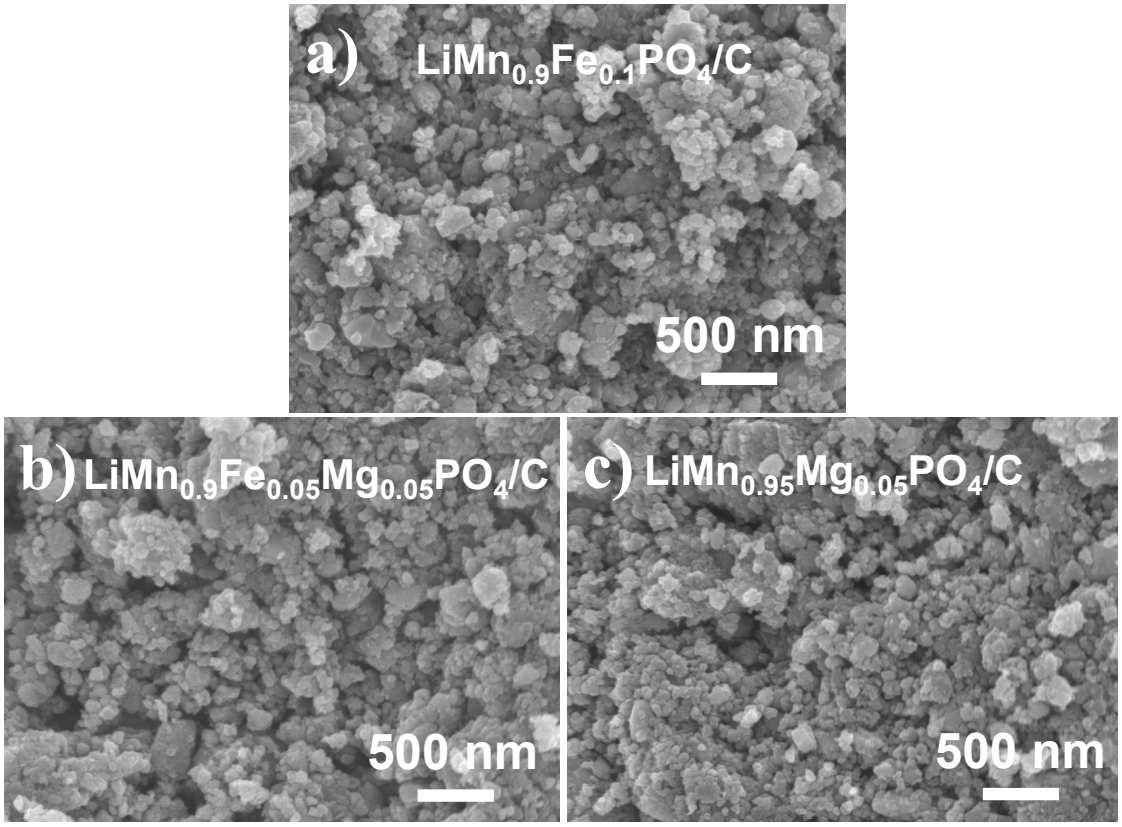

Fig. S1 FESEM images of (a) $LiMn_{0.9}Fe_{0.1}PO_4$, (b) $LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$ and (c) $LiMn_{0.95}Mg_{0.05}PO_4$.

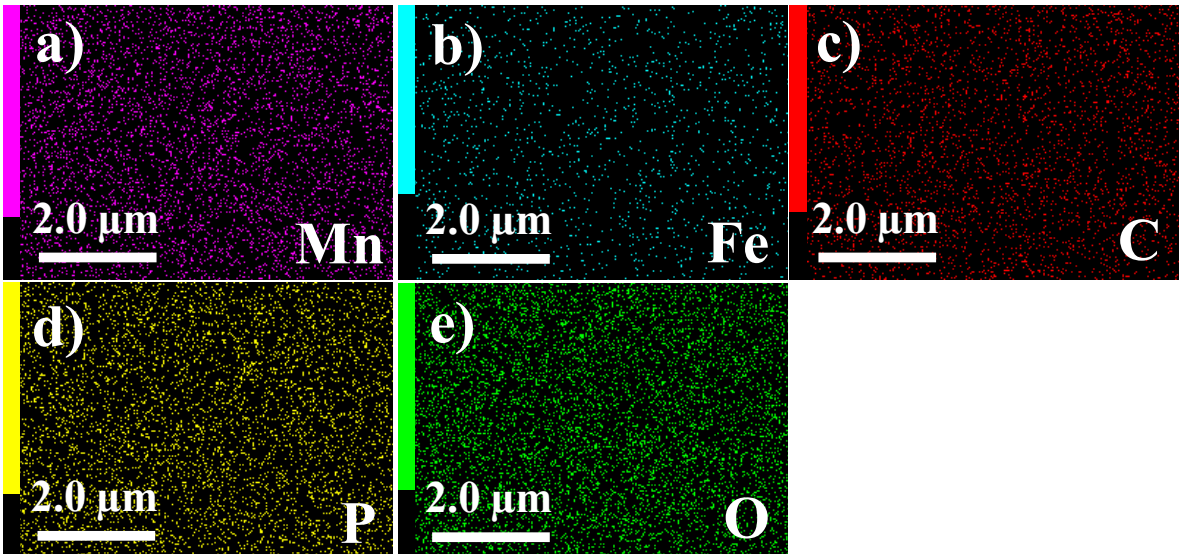

Fig. S2 Elemental mapping images of (a) manganese, (b) iron, (c) carbon, (d) phosphorus, and (e) oxygen in $LiMn_{0.9}Fe_{0.1}PO_4/C$.

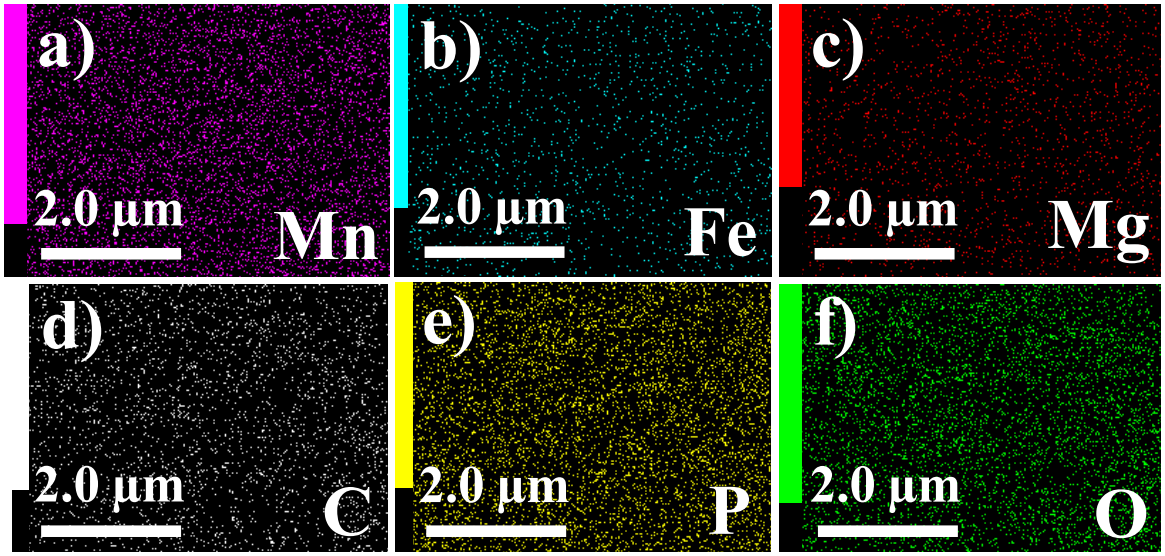

Fig. S3 Elemental mapping images of (a) manganese, (b) iron, (c) magnesium, (d) carbon, (e) phosphorus, and (f) oxygen in $LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4/C$.

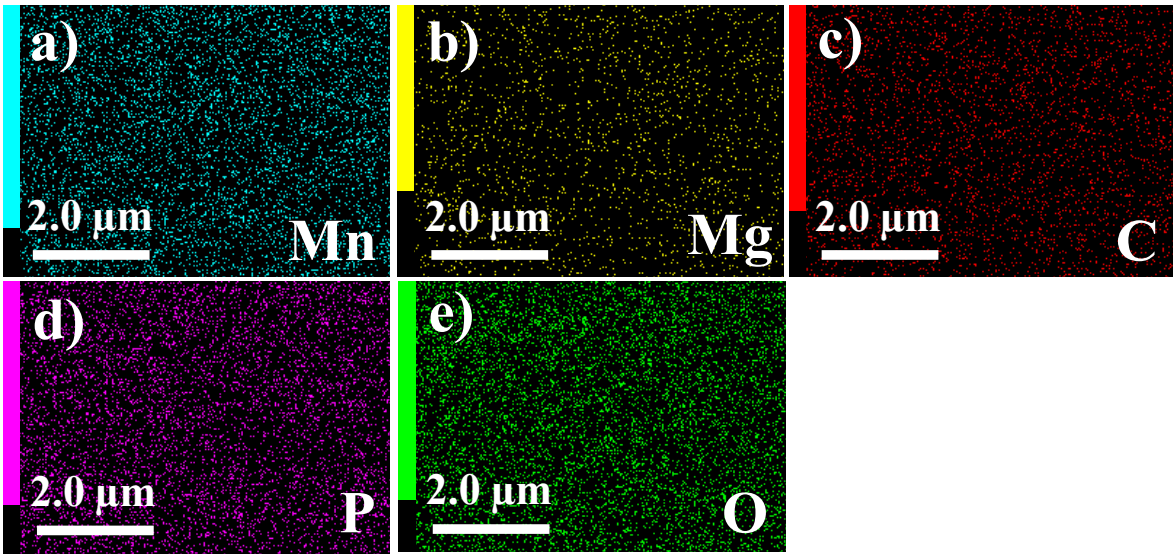

Fig. S4 Elemental mapping images of (a) manganese, (b) magnesium, (c) carbon, (d) phosphorus, and (e) oxygen in $LiMn_{0.95}Mg_{0.05}PO_4/C$.

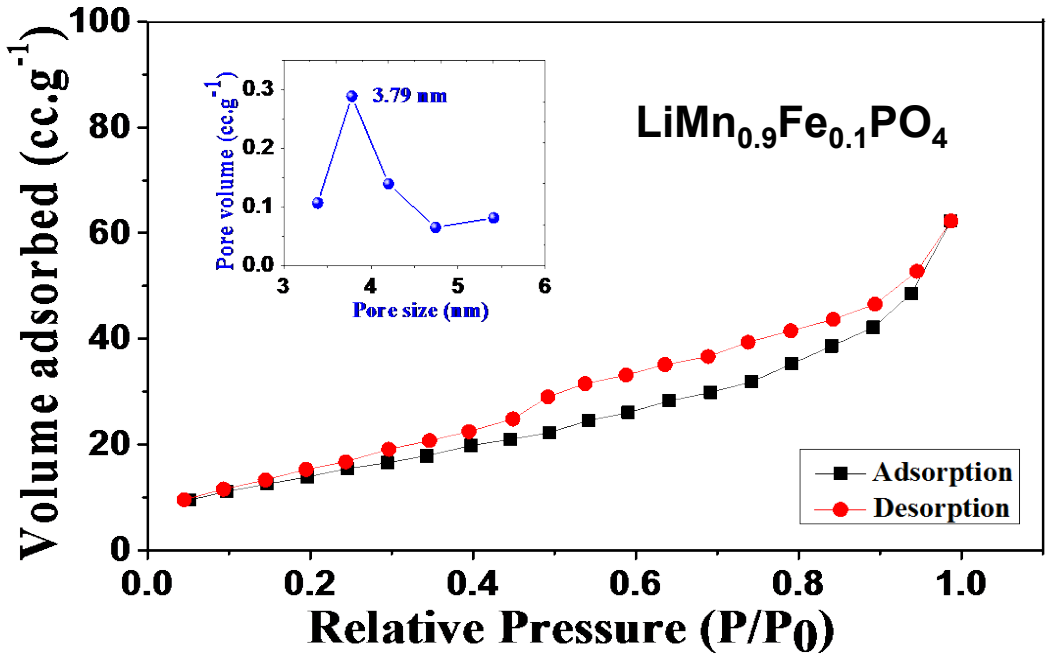

Fig. S5 Nitrogen sorption isotherm with pore size distribution (inset) for $LiMn_{0.9}Fe_{0.1}PO_4/C$.

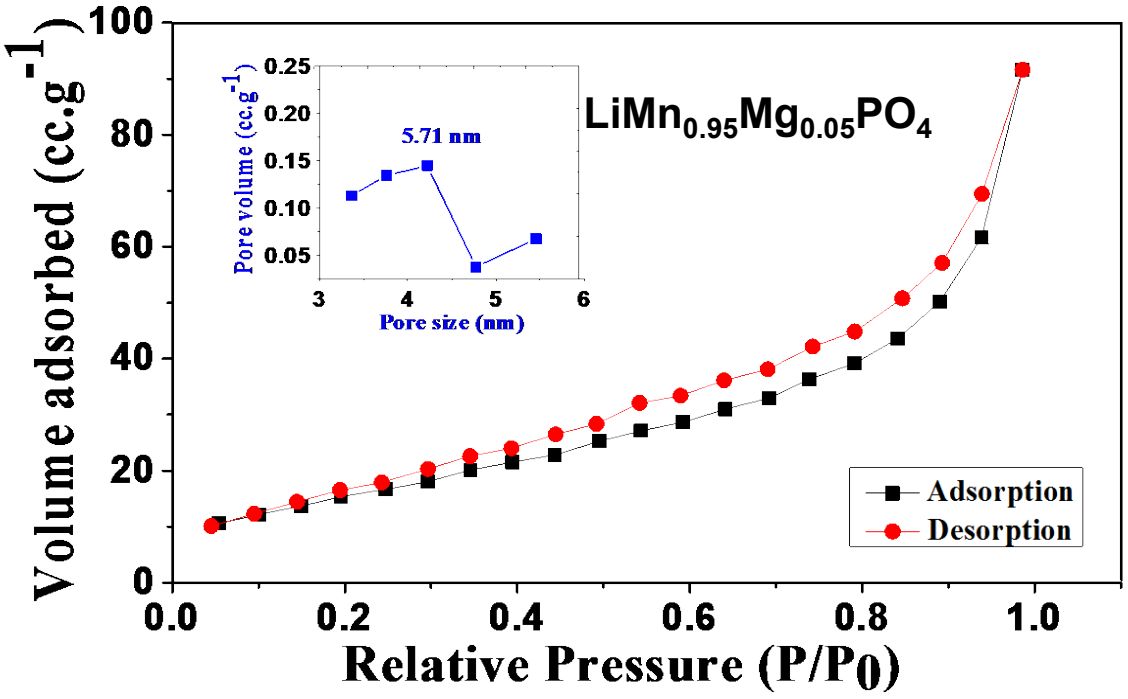

Fig. S6 Nitrogen sorption isotherm with pore size distribution (inset)for $LiMn_{0.95}Mg_{0.05}PO_4/C$.

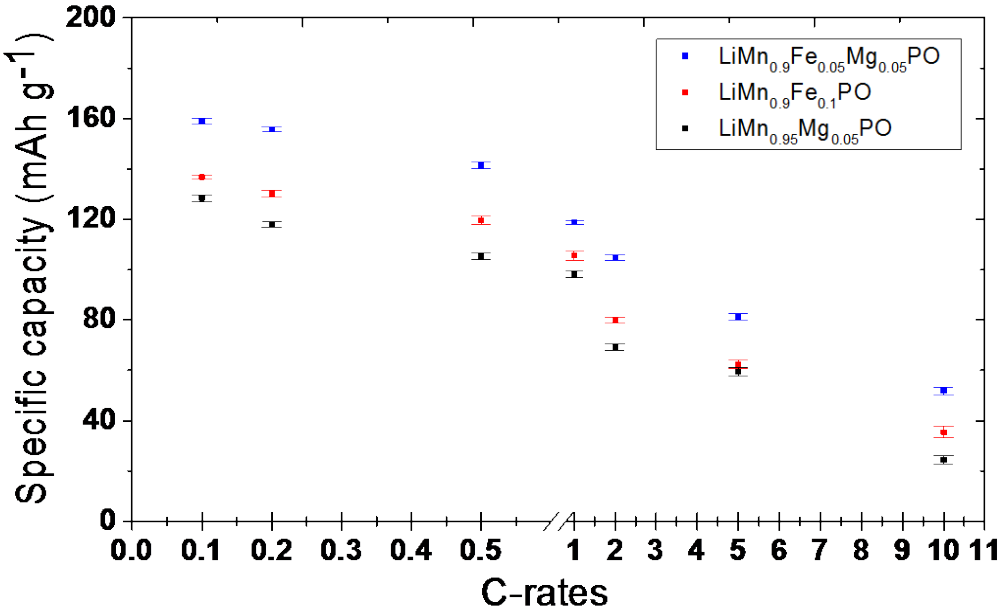

Fig. S7 Capacity error bar chart; specific capacities vs. C-rates of $LiMn_{0.9}Fe_{(0.1-x)}Mg_xPO_4/C$ (x = 0 and 0.05) and $LiMn_{0.95}Mg_{0.05}PO_4/C$.

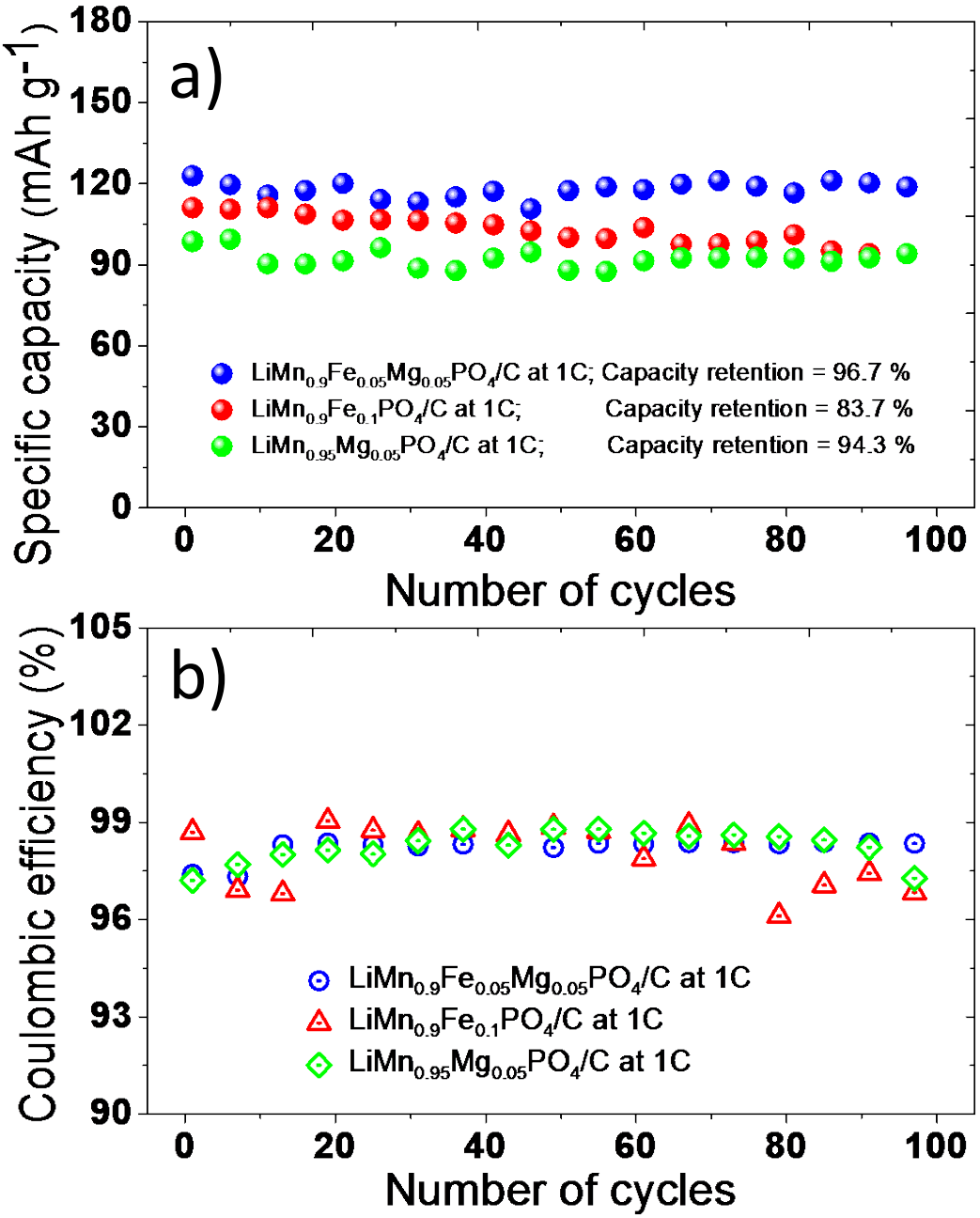

Fig. S8 (a) Capacity retention upto 100 cycles at 1C and (b) corresponding coulombic efficiency (shown in the magnified scale for the sake of clarity) of $LiMn_{0.9}Fe_{(0.1-x)}Mg_xPO_4/C$ (x = 0 and 0.05) and $LiMn_{0.95}Mg_{0.05}PO_4/C$.

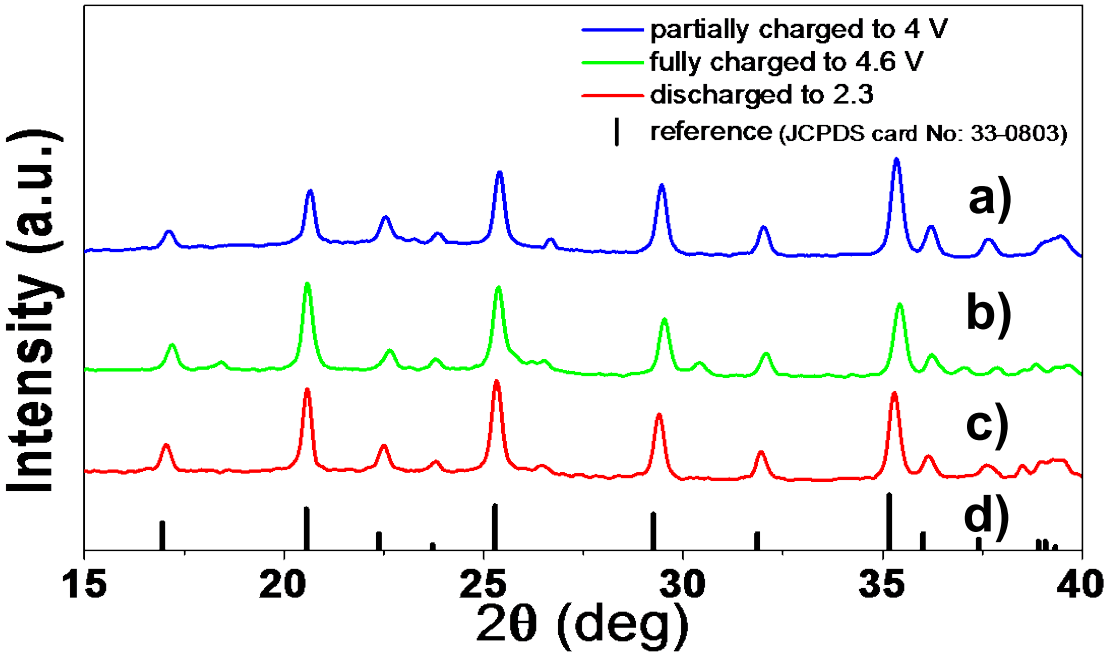

Fig. S9 Ex-situ PXRD patterns of $LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$ (a) fully charged to 4 V, (b) partially charged to 4.6 V, (c) discharged to 2.3 V and (d) standard powder pattern of $LiMnPO_4$ (JCPDS card No: 33-0803).

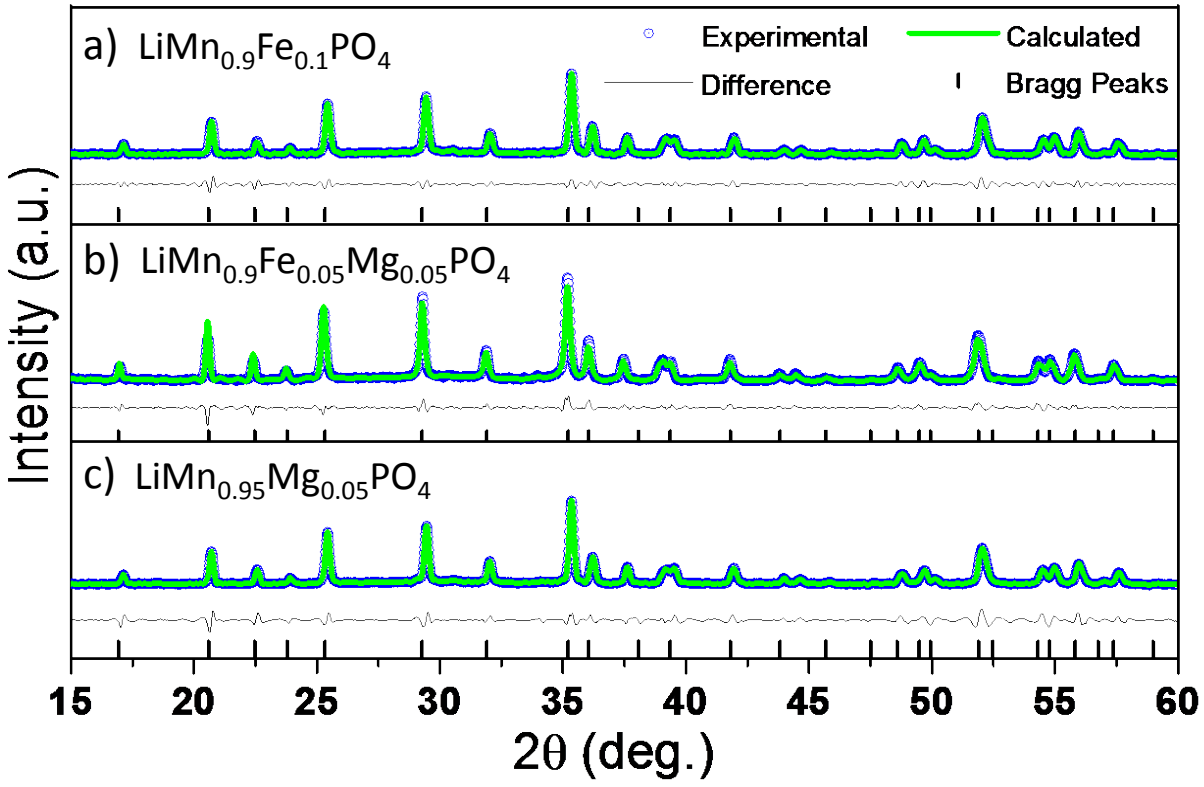

Fig. S10 Rietveld refinement of (a) $LiMn_{0.9}Fe_{0.1}PO_4$ (R_{exp}:4.91, R_{wp}:1.04 and R_p:0.61), (b) $LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$ (R_{exp}:6.77, R_{wp}:1.65 and R_p:0.99) and (c) $LiMn_{0.95}Mg_{0.05}PO_4$ (R_{exp}:6.79, R_{wp}:1.71 and R_p:1.08).

Table S1 Site occupancies of $LiMn_{0.9}Fe_{(0.1-x)}Mg_xPO_4/C$ (x = 0 and 0.05), $LiMn_{0.95}Mg_{0.05}PO_4/C$. Data for $LiMnPO_4/C$ is given for the sake comparison, whose Mn, P and O refined positions are consistent with literature report.[36, 42, 43]

$LiMnPO_4$ (R_{exp} : 11.24 R_{wp} : 4.04 R_p : 3.21)						
Atom	Site	x	y	z	Occupancy (theoretical)	Occupancy (Observed)
Li1 (Li^{+1})	4a	0.0	0.0	0.0	1	1
Mn1(Mn^{+2})	4c	0.2500	0.2817	-0.0281	1	1
P1(P^{+5})	4c	0.2500	0.0923	0.4081	1	1
O1(O^{-2})	4c	0.2500	0.0968	-0.2664	1	1
O2(O^{-2})	4c	0.2500	0.4561	0.2073	1	1
O3(O^{-2})	8d	0.0492	0.1609	0.2781	1	1
$LiMn_{0.9}Fe_{0.1}PO_4$ (R_{exp} : 4.91 R_{wp} : 1.04 R_p : 0.61)						
Atom	Site	x	y	z	Occupancy (theoretical)	Occupancy (Observed)
Li1 (Li^{+1})	4a	0.0	0.0	0.0	1	0.9994
Li2 (Li^{+1})	4c	0.2500	0.2817	-0.0281	0	0.0006
Fe1(Fe^{+2})	4a	0.0	0.0	0.0	0	0.0006
Fe2(Fe^{+2})	4c	0.2500	0.2817	-0.0281	0.1	0.0994
Mn1(Mn^{+2})	4c	0.2500	0.2817	-0.0281	0.90	0.90
P1(P^{+5})	4c	0.2500	0.0923	0.4081	1	1
O1(O^{-2})	4c	0.2500	0.0968	-0.2664	1	1
O2(O^{-2})	4c	0.2500	0.4561	0.2073	1	1
O3(O^{-2})	8d	0.0492	0.1609	0.2781	1	1

$LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$ (R_{exp} : 6.77 R_{wp} : 1.65 R_p : 0.99)						
Atom	Site	x	y	z	Occupancy (theoretical)	Occupancy (Observed)
Li1 (Li^{+1})	4a	0.0	0.0	0.0	1	0.9987
Li2 (Li^{+1})	4c	0.2500	0.2817	-0.0281	0	0.0013
Mg1(Mg^{+2})	4a	0.0	0.0	0.0	0	0.0013
Mg2(Mg^{+2})	4c	0.2500	0.2817	-0.0281	0.05	0.0487
Fe2(Fe^{+2})	4c	0.2500	0.2817	-0.0281	0.05	0.05
Mn1(Mn^{+2})	4c	0.2500	0.2817	-0.0281	0.90	0.90
P1(P^{+5})	4c	0.2500	0.0923	0.4081	1	1
O1(O^{-2})	4c	0.2500	0.0968	-0.2664	1	1
O2(O^{-2})	4c	0.2500	0.4561	0.2073	1	1
O3(O^{-2})	8d	0.0492	0.1609	0.2781	1	1
$LiMn_{0.95}Mg_{0.05}PO_4$ (R_{exp} : 6.79 R_{wp} : 1.71 R_p : 1.08)						
Atom	Site	x	y	z	Occupancy (theoretical)	Occupancy (Observed)
Li1 (Li^{+1})	4a	0.0	0.0	0.0	1	0.9986
Li2 (Li^{+1})	4c	0.2500	0.2817	-0.0281	0	0.0014
Mg1(Mg^{+2})	4a	0.0	0.0	0.0	0	0.0014
Mg2(Mg^{+2})	4c	0.2500	0.2817	-0.0281	0.05	0.0486
Mn1(Mn^{+2})	4c	0.2500	0.2817	-0.0281	0.95	0.95
P1(P^{+5})	4c	0.2500	0.0923	0.4081	1	1
O1(O^{-2})	4c	0.2500	0.0968	-0.2664	1	1
O2(O^{-2})	4c	0.2500	0.4561	0.2073	1	1
O3(O^{-2})	8d	0.0492	0.1609	0.2781	1	1

We have carried out XRD refinement to check the position of dopants (Fe^{2+} and/or Mg^{2+}) by Rietveld refinement using TOPAS 3.0 version. The quality of the refinement and dopant position was determined based on R_{exp}, R_{wp}, and R_p values. For instance in the case of $LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$ firstly, assuming the Mg^{2+} and Fe^{2+} occupy only Li sites, the reliability factor were R_{exp}:6.77, R_{wp}:1.83 and R_p:1.10; Secondly, assuming the Mg^{2+} and Fe^{2+} occupy only Mn sites, then the reliability factors R_{exp}:6.77, R_{wp}:1.80 and R_p:1.07; Thirdly, assuming the Mg^{2+} and Fe^{2+} occupy simulteneoualy both Li and Mn sites, then the reliability factors are R_{exp}:6.77, R_{wp} : 1.65 and R_p:0.99. Based on good reliability factors as seen from the third case and observed site occupancies as shown in Table S1, Mg^{2+} and Fe^{2+} are most likely to occupy Mn sites. Under these lines, $LiMn_{0.9}Fe_{0.1}PO_4$ and $LiMn_{0.95}Mg_{0.05}PO_4$ are also refined based on above three possibilities. Similarly, we found that Fe^{2+} or Mg^{2+} occupy simulteneoualy both Li and Mn sites as inferred from the better reliability factors (R_{exp}:4.91, R_{wp}:1.04 and R_p:0.61 for $LiMn_{0.9}Fe_{0.1}PO_4$; R_{exp}:6.79, R_{wp}:1.71 and R_p:1.08 for $LiMn_{0.95}Mg_{0.05}PO_4$). Hence, as seen from the site occupancies in all the samples (Table S1) from Rietveld refinement, Fe^{2+} and/or Mg^{2+} is found to be substituted mostly in the Mn site , not in the Li site.

Table S2 Nitrogen sorption data of $LiMn_{0.9}Fe_{(0.1-x)}Mg_xPO_4/C$ (x = 0 and 0.05) and $LiMn_{0.95}Mg_{0.05}PO_4/C$

Nitrogen sorption data of Fe^{2+} and/or Mg^{2+} doped $LiMnPO_4$	$LiMn_{0.9}Fe_{0.1}PO_4$	$LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$	$LiMn_{0.95}Mg_{0.05}PO_4$
Surface Area (S_{BET}) ($m^2.g^{-1}$) (±2)	45	52	48
Pore volume ($cc.g^{-1}$) (±0.0005)	0.084	0.132	0.1
Pore size (nm) (±0.1)	3.7	3.7	5.7

***S_{BET} – Surface area by Brunauer–Emmet–Teller equation; S_t –Surface area derived from V–t plot.**

Table S3 A summary of lithium storage performance of all the composition at different current rates.

Electrode materials/ C rates	0.1C	0.2C	0.5C	1C	2C	5C	10C
$LiMn_{0.9}Fe_{0.1}PO_4$	136.8	130.2	119.6	105.6	80	62.4	35.4
$LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$	159	155.8	141.4	118.8	104.6	81.4	51.8
$LiMn_{0.95}Mg_{0.05}PO_4$	128.4	118	105.2	98.2	69.2	59.4	24.4

Table S4 A summary of lithium storage performance and carbon content from the literature.

S.N	Electrode composition	Carbon content	Maximum Capacity (in mAh g^{-1})	References
1	$LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$/C	25wt % carbon	159	Present work
2	$LiMn_{0.9}Mg_{0.1}PO_4$/C	25wt % carbon + 5 % synthetic flake graphite	120	31
3	$LiMn_{0.99}Mg_{0.01}PO_4$/C	25wt % carbon	145	32
4	$LiMn_{0.8}Mg_{0.2}PO_4$/C	25wt % carbon + 5 % synthetic flake graphite	150	34
5	$LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$/C	31wt % carbon	140	36
6	$LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4$/C	20wt % carbon	140	37
7	$LiMn_{0.8}Mg_{0.2}PO_4$/C	12.1wt % carbon +8wt % synthetic flake graphite	70	40