Supplementary Information

Multi-element doping design for a high-performance $LiMnPO_4$ cathode via metaheuristics computation

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Table S1. Transition metal precursors for 11 dopants.

Dopant	Precursor	Manufacturer
Al	$Al(NO_3)_3 \cdot 9H_2O$, 99.997%	Aldrich
Ca	$Ca(NO_3)_2 \cdot 4H_2O$, 99%	Sigma-Aldrich
Co	$Co(CH_3COO)_2 \cdot 4H_2O$, 98%	Sigma-Aldrich
Cu	$CuCl_2$, 99.999%	Aldrich
Fe	$FeC_2O_4 \cdot 2H_2O$, 99%	Alfa Aesar
Mg	$Mg(NO_3)_2 \cdot 6H_2O$, 99.999%	Aldrich
Ni	$Ni(CH_3COO)_2 \cdot 4H_2O$, 99.998%	Aldrich
Ti	$Ti(OC_3H_7)_4$, 98%	Aldrich
Y	$Y(NO_3)_3 \cdot 6H_2O$, 99.8%	Aldrich
Zn	$Zn(CH_3COO)_2$, 99.99%	Aldrich
Zr	$Zr[O(CH_2)_3CH_3]_4$ solution (80 wt.% in 1-butanol)	Aldrich

Figure S1. Dopants composition and battery performance results of 150 cathode samples.

1st generation

sample #	Dopant1	Dopant2	Dopant3	D1 (wt.%)	D2 (wt.%)	D3 (wt.%)	C-rate (%)	Capacity (mAh g^{-1})	Cyclability (%)
1	Ca	Zn	Al	1.2	1.0	2.4	66.09	121	94.85
2	Cu	Zn	Al	1.0	1.8	2.4	75.68	127	92.69
3	Fe	Ni	Ti	1.2	1.4	1.4	74.56	116	93.63
4	Co	Fe	Ni	2.0	2.2	1.2	71.46	124	93.74
5	Co	Fe	Zr	2.2	2.6	2.6	72.10	122	86.18
6	Ca	Fe	Y	1.2	1.4	2.6	77.79	118	97.76
7	Fe	Ni	Y	1.6	2.2	2.4	70.72	125	93.68
8	Mg	Co	Ni	1.2	1.2	1.4	75.61	131	92.15
9	Mg	Ni	Ti	1.4	1.2	2.4	67.47	129	92.85
10	Ni	Y	Zr	1.0	1.6	1.0	69.89	124	91.46
11	Co	Fe	Zr	1.6	2.2	1.0	64.98	133	94.37
12	Fe	Cu	Zr	2.0	3.0	2.2	64.34	130	82.31
13	Ca	Cu	Ti	1.4	2.2	1.6	66.16	104	89.82
14	Ca	Fe	Zr	2.2	1.4	2.4	64.84	133	82.86
15	Mg	Cu	Ti	1.6	1.8	2.4	75.77	133	97.86
16	Co	Ni	Ti	1.0	2.4	1.4	75.03	126	94.05
17	Ca	Ni	Zn	1.4	3.0	1.2	72.64	119	92.17
18	Co	Cu	Ni	2.2	1.4	1.2	66.42	122	90.89
19	Ca	Fe	Zn	2.2	2.2	2.2	65.31	128	94.84
20	Co	Ni	None	1.4	1.6	0.0	74.30	122	91.40
21	Co	Cu	Y	2.2	3.0	2.4	53.57	131	84.35
22	Cu	Ni	Y	1.6	1.8	2.6	68.41	124	89.24
23	Ni	Zn	Al	1.2	2.2	1.4	66.38	121	90.98
24	Mg	Fe	Y	1.8	2.2	1.2	62.94	121	95.80
25	Zn	Y	Zr	1.0	1.0	2.4	69.57	118	88.27

2nd generation

sample #	Dopant1	Dopant2	Dopant3	D1 (wt.%)	D2 (wt.%)	D3 (wt.%)	C-rate (%)	Capacity (mAh g^{-1})	Cyclability (%)
1	Fe	Y	None	1.8	1.6	0.0	56.53	125	97.11
2	Cu	Y	Ti	2.4	1.6	1.8	66.16	104	89.45
3	Co	Ni	None	1.4	2.8	0.0	79.63	133	90.12
4	Ca	Fe	Y	1.2	1.2	1.6	48.71	123	92.35
5	Co	Ni	Ti	1.0	2.4	1.8	65.40	126	91.74
6	Ca	Ni	Zn	1.4	2.8	2.8	70.08	127	92.56
7	Ca	Fe	Y	1.6	2.0	1.0	59.76	131	97.52
8	Mg	Co	Ni	1.2	1.4	1.8	64.04	131	93.86
9	Co	Cu	Y	1.0	1.0	2.4	41.55	112	77.34
10	Co	Ni	Zr	1.4	1.4	2.6	62.62	130	87.49
11	Co	Y	Zr	1.0	1.8	2.0	53.51	123	89.18
12	Cu	Zn	Al	1.0	1.8	1.6	64.41	124	90.62
13	Co	Cu	Ni	2.2	1.4	1.6	65.46	131	91.18
14	Mg	Co	Ni	1.2	1.2	1.6	70.64	140	90.79
15	Ni	Zn	Al	1.2	2.2	1.2	73.00	134	93.85
16	Co	Fe	Ni	2.0	2.4	2.6	70.20	141	93.82
17	Fe	Ni	Zn	1.2	1.0	1.8	68.65	137	90.27
18	Ni	Zn	Zr	1.6	1.2	1.8	64.50	138	86.71
19	Ca	Al	Y	2.0	1.8	1.2	56.22	123	88.58
20	Ni	Zn	Al	1.2	2.0	3.0	51.77	113	77.08
21	Co	Fe	Zr	1.6	2.8	1.0	66.97	132	89.44
22	Cu	Zn	Y	1.2	1.8	3.0	52.41	109	78.98
23	Ca	Fe	Y	2.2	2.4	2.0	61.21	121	93.73
24	Cu	Zn	Al	1.6	2.4	2.8	51.56	119	83.88
25	Mg	Ca	None	1.0	1.0	0.0	62.57	113	93.29

3rd generation

sample #	Dopant1	Dopant2	Dopant3	D1 (wt.%)	D2 (wt.%)	D3 (wt.%)	C-rate (%)	Capacity (mAh g^{-1})	Cyclability (%)
1	Co	Ni	None	1.4	2.6	0.0	69.51	127	87.19
2	Co	Fe	Zr	1.8	2.4	2.8	72.45	121	87.85
3	Co	Cu	Zr	2.4	2.0	1.4	58.53	125	84.40
4	Cu	Al	Y	1.8	1.2	2.4	64.89	125	86.28
5	Co	Fe	Zr	1.6	2.8	1.2	65.56	131	92.28
6	Fe	Y	None	2.0	2.2	0.0	67.58	126	90.55
7	Ca	Fe	Zn	2.4	1.2	2.6	67.47	136	87.61
8	Cu	Y	Zr	1.8	1.6	1.0	74.77	132	85.69
9	Ca	Fe	Y	1.2	1.4	2.4	76.17	131	89.99
10	Mg	Co	Ti	1.8	1.2	1.6	63.84	132	89.84
11	Co	Fe	Zn	2.2	2.0	1.6	61.42	128	84.58
12	Ca	Fe	Y	1.6	2.2	2.8	56.07	130	87.05
13	Ca	Fe	Y	1.6	1.0	1.4	64.25	134	82.85
14	Ca	Fe	Zn	2.2	1.6	2.6	57.03	125	93.54
15	Ca	Ni	Zn	1.4	3.0	1.6	66.56	133	87.07
16	Co	Cu	Zr	1.8	1.2	1.4	54.91	128	85.99
17	Ca	Fe	Ni	1.4	2.8	2.8	72.03	134	92.64
18	Mg	Co	Zn	1.8	1.0	1.6	67.76	137	86.67
19	Co	Fe	Zn	1.0	1.4	2.6	62.96	142	90.62
20	Mg	Co	Ni	2.4	1.6	1.8	72.96	141	91.76
21	Ca	Ni	Zn	1.4	2.6	2.8	54.96	142	87.87
22	Mg	Co	Ni	1.4	1.0	1.0	63.67	136	90.05
23	Co	Fe	Ni	2.0	2.4	2.8	72.39	140	94.16
24	Ni	Zn	Zr	1.2	3.0	1.4	66.76	143	86.70
25	Fe	Zn	Al	2.2	2.4	1.6	67.95	140	89.57

4th generation

sample #	Dopant1	Dopant2	Dopant3	D1 (wt.%)	D2 (wt.%)	D3 (wt.%)	C-rate (%)	Capacity (mAh g^{-1})	Cyclability (%)
1	Co	Fe	Zr	1.6	3.0	1.4	68.96	124	94.90
2	Cu	Zn	None	1.6	2.0	0.0	59.40	120	89.93
3	Ni	Zn	Al	1.2	2.4	2.0	69.15	127	89.30
4	Co	Fe	Zn	1.4	1.6	1.0	60.83	131	92.66
5	Co	Fe	Ni	1.6	2.2	2.0	65.19	128	92.90
6	Ca	Zn	Zr	1.2	2.6	2.6	64.51	124	89.48
7	Ca	Fe	Zn	2.0	1.0	2.2	65.62	130	85.76
8	Co	Fe	Zr	1.6	2.8	2.0	69.36	141	92.38
9	Ca	Zn	Al	1.4	3.0	1.4	71.00	132	87.66
10	Mg	Co	Zn	1.6	3.0	2.4	67.34	131	87.22
11	Co	Cu	Y	1.8	2.6	1.6	62.54	136	83.80
12	Ca	Fe	Zn	2.4	1.0	1.2	60.65	128	88.27
13	Co	Fe	Zn	1.0	1.2	1.0	66.99	130	90.36
14	Ni	Zn	Al	1.2	2.4	1.2	71.75	133	88.24
15	Mg	Co	Ni	1.2	2.8	2.2	68.63	137	92.17
16	Fe	Y	Ti	1.2	2.2	1.8	67.34	126	91.93
17	Ca	Zn	Y	1.2	2.2	2.0	62.84	129	92.33
18	Mg	Co	Ni	2.4	1.6	2.2	73.00	147	91.39
19	Mg	Co	Zn	1.8	1.0	1.4	66.84	146	88.03
20	Ca	Fe	Zn	2.4	1.4	3.0	64.61	133	91.17
21	Co	Ni	None	1.2	2.6	0.0	75.43	143	91.54
22	Ca	Cu	Y	1.6	1.0	2.8	67.43	134	90.24
23	Co	Fe	Y	1.0	1.8	1.8	70.60	137	94.35
24	Co	Y	None	1.6	1.8	0.0	75.64	136	90.04
25	Ca	Ni	Zn	1.4	2.4	2.0	74.71	142	89.17

5th generation

sample #	Dopant1	Dopant2	Dopant3	D1 (wt.%)	D2 (wt.%)	D3 (wt.%)	C-rate (%)	Capacity (mAh g^{-1})	Cyclability (%)
1	Cu	Zn	Ti	1.2	2.2	2.6	66.76	125	94.95
2	Ca	Fe	Ti	1.0	2.0	1.0	64.22	126	94.99
3	Mg	Co	Zn	1.8	1.0	1.2	74.89	125	95.44
4	Cu	Y	Zr	1.8	1.6	1.4	62.87	122	93.16
5	Ca	Ni	Zn	1.4	3.0	1.4	72.17	129	88.33
6	Ca	Fe	Ni	1.4	2.8	3.0	64.36	127	85.84
7	Ca	Fe	Al	1.0	2.0	1.6	68.16	124	97.08
8	Cu	Zr	None	1.6	2.2	0.0	59.28	113	85.44
9	Mg	Co	Zr	1.4	1.4	1.4	65.37	123	94.02
10	Cu	Y	Zr	1.8	1.8	2.4	65.04	125	95.29
11	Ca	Ni	Zn	1.4	2.2	1.0	82.85	117	94.30
12	Co	Y	None	1.4	3.0	0.0	66.33	129	93.25
13	Co	Al	Zr	1.2	2.0	2.0	64.95	116	92.31
14	Mg	Co	Cu	1.8	1.0	1.6	64.23	131	93.73
15	Ni	Al	Y	1.8	2.2	1.2	67.50	128	94.24
16	Ca	Fe	Y	2.2	2.4	2.0	55.92	124	85.08
17	Ni	Zn	Al	1.2	2.6	3.0	81.55	124	94.64
18	Ca	Ni	Zn	1.6	1.4	2.0	63.29	124	91.73
19	Co	Fe	Zn	2.2	1.8	3.0	78.70	135	92.91
20	Co	Fe	Al	2.4	1.4	1.0	80.72	129	93.38
21	Cu	Ni	Ti	1.6	2.2	2.8	61.21	120	86.75
22	Ca	Fe	Zn	2.4	1.2	2.8	73.28	138	87.31
23	Mg	Co	Cu	1.8	1.2	2.6	70.97	129	92.00
24	Co	Fe	Ti	2.2	2.6	1.2	60.35	134	84.71
25	Cu	Zn	Ti	1.4	2.0	1.2	69.24	138	88.83

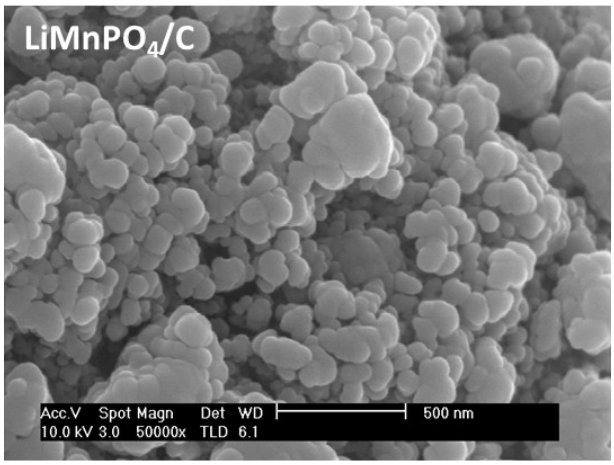
6th generation

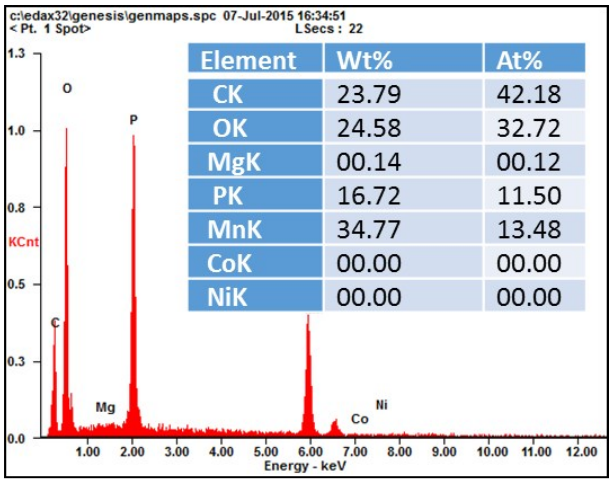
sample #	Dopant1	Dopant2	Dopant3	D1 (wt.%)	D2 (wt.%)	D3 (wt.%)	C-rate (%)	Capacity (mAh g^{-1})	Cyclability (%)
1	Co	Fe	Zn	2.2	2.0	1.4	66.70	122	85.65
2	Mg	Co	Zn	1.4	2.2	2.8	82.56	129	90.19
3	Cu	Zn	Ti	1.4	2.0	2.6	76.77	129	91.58
4	Ca	Fe	Al	1.6	2.0	1.8	78.30	127	96.07
5	Cu	Zn	Ti	1.4	1.6	2.4	77.26	124	94.44
6	Co	Fe	Zn	2.2	2.0	1.0	69.88	135	96.67
7	Co	Fe	Zr	1.6	2.6	2.8	78.81	133	91.79
8	Co	Fe	Al	2.2	2.6	3.0	67.69	120	95.82
9	Mg	Co	Cu	1.8	1.2	2.4	67.86	137	88.56
10	Mg	Co	Ni	1.6	1.2	1.0	72.05	133	93.58
11	Ca	Cu	Y	1.6	1.0	3.0	61.33	127	87.20
12	Cu	Zn	Ti	1.2	2.4	2.0	66.84	134	91.36
13	Co	Fe	Al	2.4	1.8	1.2	54.53	113	86.77
14	Co	Fe	Ni	1.4	3.0	1.0	51.88	121	84.50
15	Mg	Fe	Al	1.2	1.0	2.0	52.95	119	85.58
16	Mg	Cu	Ti	1.2	3.0	2.8	57.43	120	88.43
17	Co	Cu	Zr	2.4	1.8	2.4	67.58	127	86.94
18	Co	Ni	None	1.2	2.4	0.0	68.04	127	94.60
19	Fe	Cu	Zr	1.4	2.8	1.6	62.43	136	86.71
20	Ca	Ni	Ti	1.0	1.0	1.8	70.62	120	94.37
21	Ca	Cu	Y	1.6	1.6	1.6	67.94	118	89.13
22	Ni	Al	Y	2.0	1.6	2.2	64.86	116	94.72
23	Co	Ni	Al	2.0	1.6	1.6	67.59	129	95.61
24	Ni	Al	Zr	1.4	2.2	2.4	55.84	122	86.03
25	Co	Fe	Zr	1.8	1.0	2.0	67.44	129	93.70

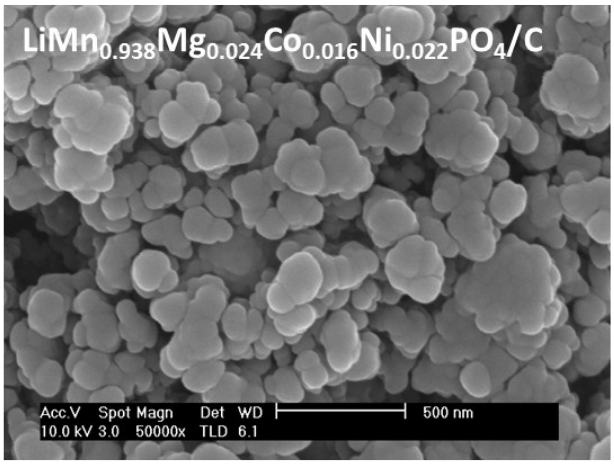
Table S2. The stoichiometric molar composition of the samples measured using ICP-AES

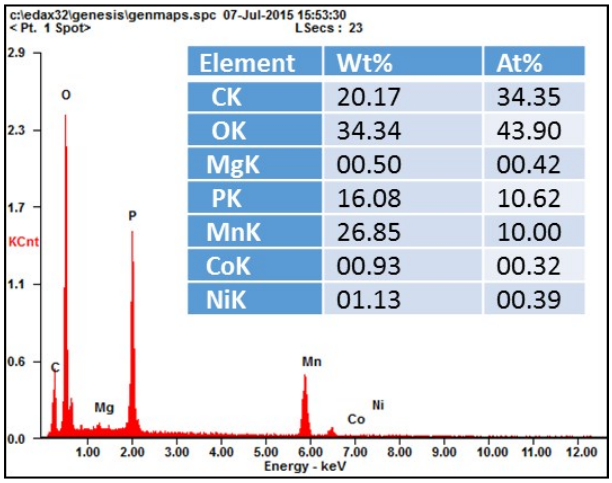
	Li	Mn	Mg	Co	Ni	P
$LiMnPO_4/C$	1.046	1.008	-	-	-	1
$LiMn_{0.938}Mg_{0.024}Co_{0.016}Ni_{0.02}PO_4/C$	1.087	0.973	0.028	0.016	0.021	1
$LiMn_{0.962}Co_{0.012}Ni_{0.026}PO_4/C$	1.048	0.976	-	0.013	0.025	1

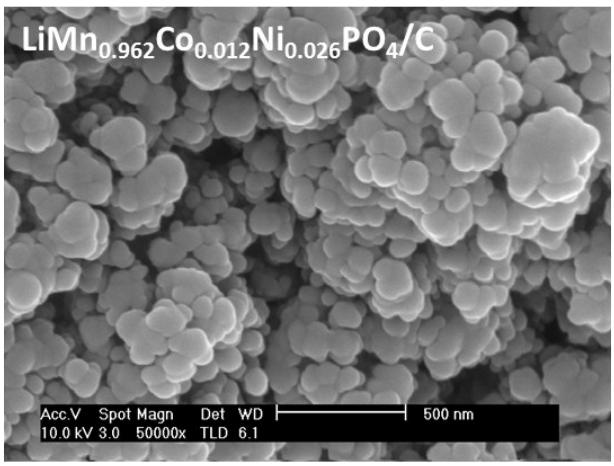
Figure S2. SEM images and atomic fractions of the samples.











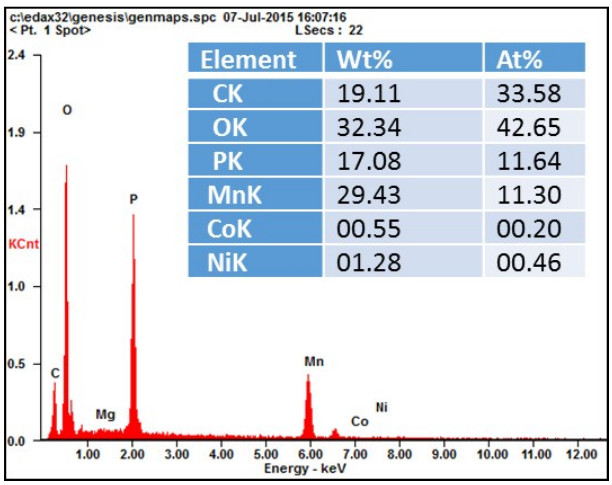


Figure S3. (a) Co K-edge XANES spectra and (b) Ni K-edge XANES spectra of $LiMn_{0.938}Mg_{0.024}Co_{0.016}Ni_{0.02}PO_4/C$ and $LiMn_{0.962}Co_{0.012}Ni_{0.026}PO_4/C$.

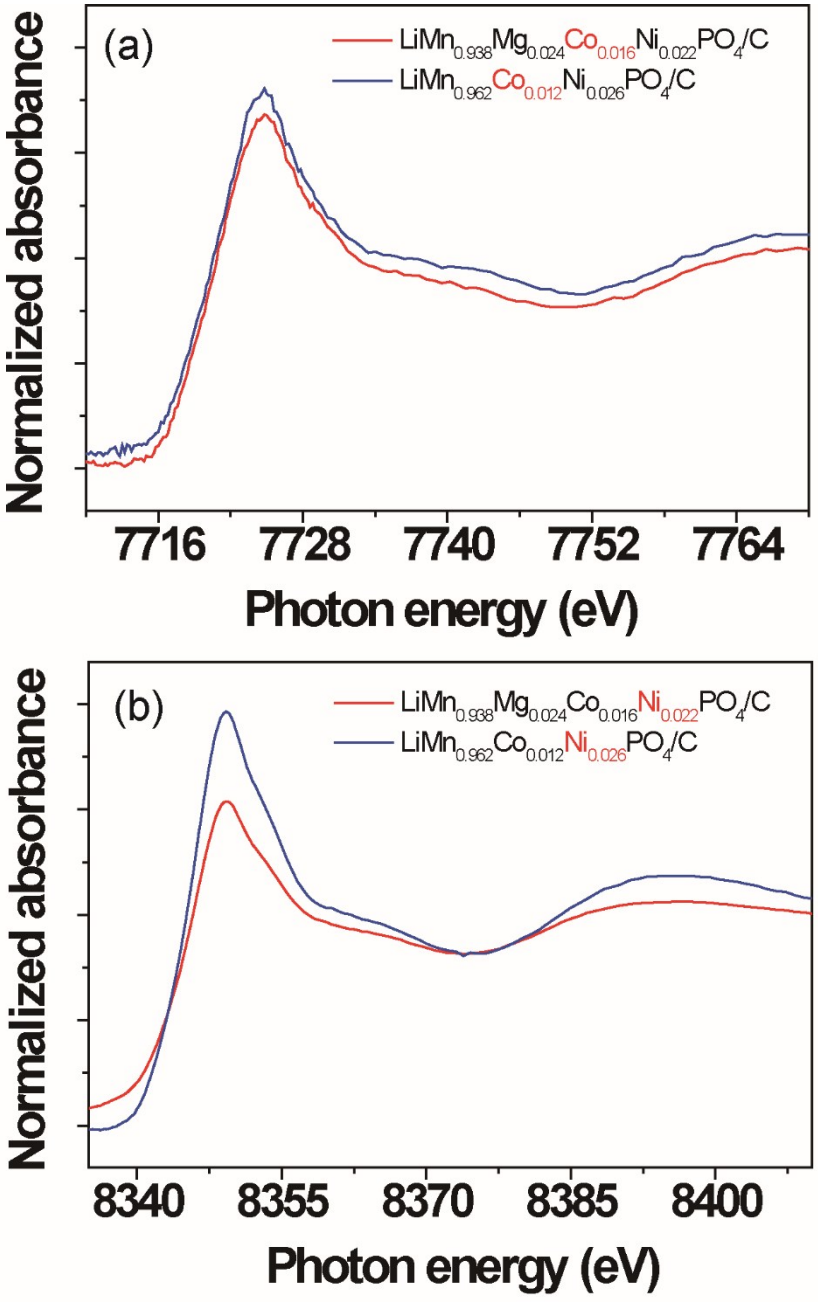


Figure S4. CV plots and the estimated R_{ct} from linear *I-V* regions for (a) $LiMnPO_4$, (b) $LiMnPO_4/C$, (c) $LiMn_{0.938}Mg_{0.024}Co_{0.016}Ni_{0.02}PO_4/C$, and (d) $LiMn_{0.962}Co_{0.012}Ni_{0.026}PO_4/C$.