

Supporting Information

Role of Local and Electronic Structural Changes with Partially Anion substitution

Lithium Manganese Spinel Oxides on Their Electrochemical Properties:

X-ray Absorption Spectroscopy Study

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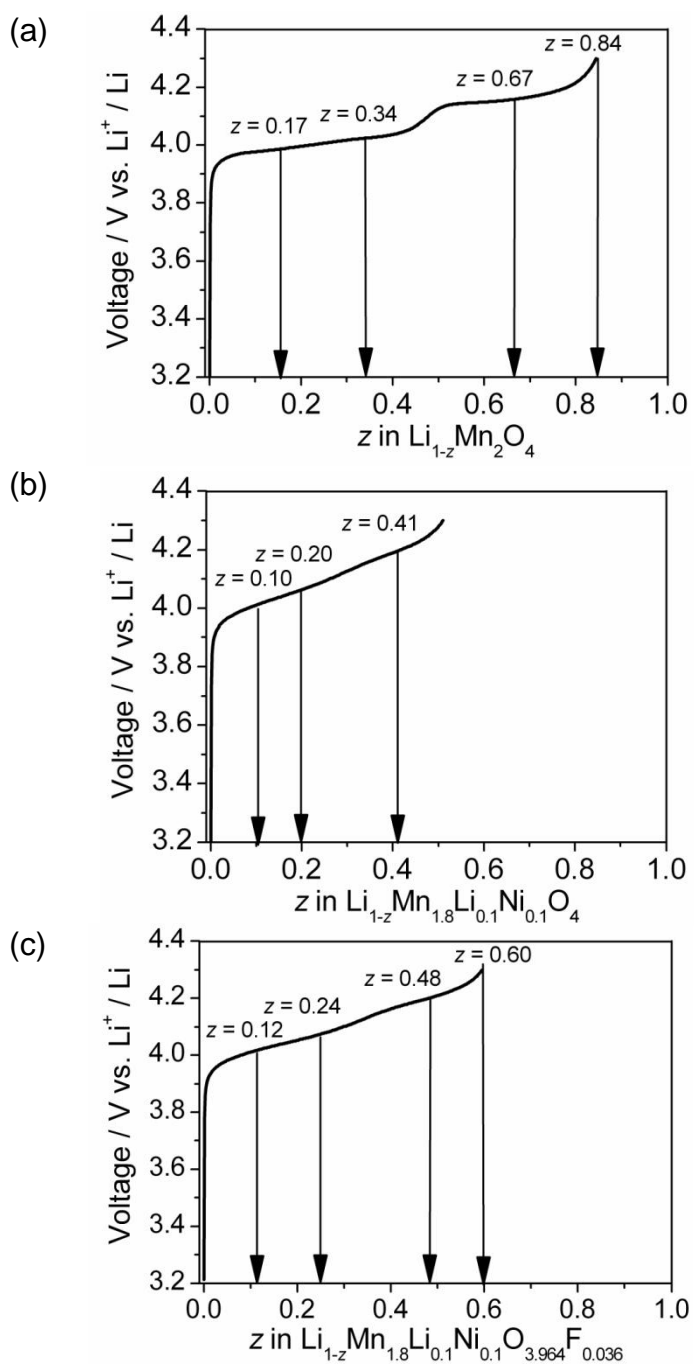


Figure S1 Electrochemical discharge profiles of $\text{Li}_{1-z}\text{Mn}_2\text{O}_4$ (a), $\text{Li}_{1-z}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_4$ (b) and $\text{Li}_{1-z}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.964}\text{F}_{0.036}$ (c) by a galvanostatic method (C rate: 1/12 C). The arrows indicate the samples for the XAFS measurements.

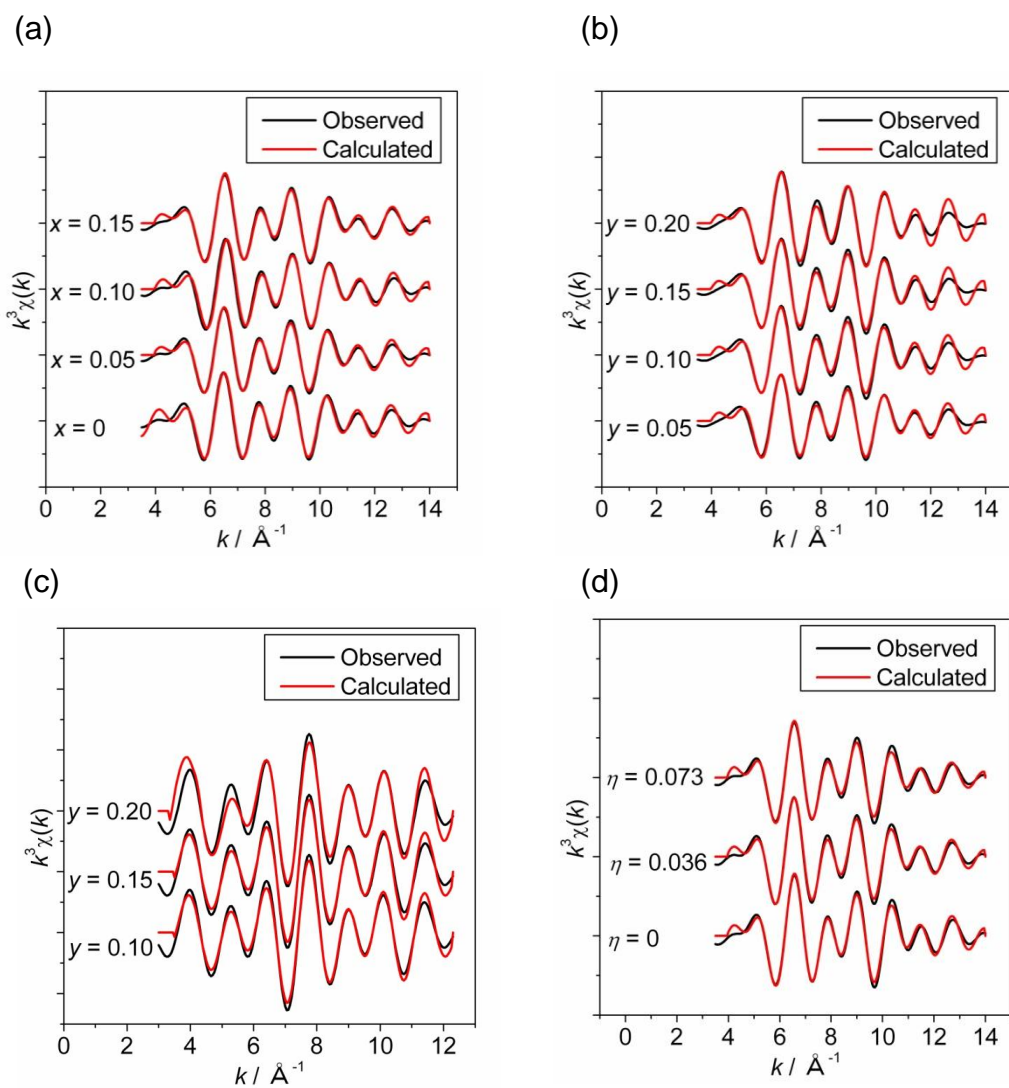


Figure S2 Curve-fitting results for inverse FT Mn K-edge EXAFS spectra of $\text{LiMn}_{2-x}\text{Li}_x\text{O}_4$ ($x = 0, 0.05, 0.10, 0.15$) (a), $\text{LiMn}_{1.9-y}\text{Li}_{0.1}\text{Ni}_y\text{O}_4$ ($y = 0.05, 0.10, 0.15, 0.20$) (b), $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-\eta}\text{F}_\eta$ ($\eta = 0, 0.036, 0.073$) (d), and inverse FT Ni K-edge EXAFS spectra of $\text{LiMn}_{1.9-y}\text{Li}_{0.1}\text{Ni}_y\text{O}_4$ ($y = 0.10, 0.15, 0.20$) (c).

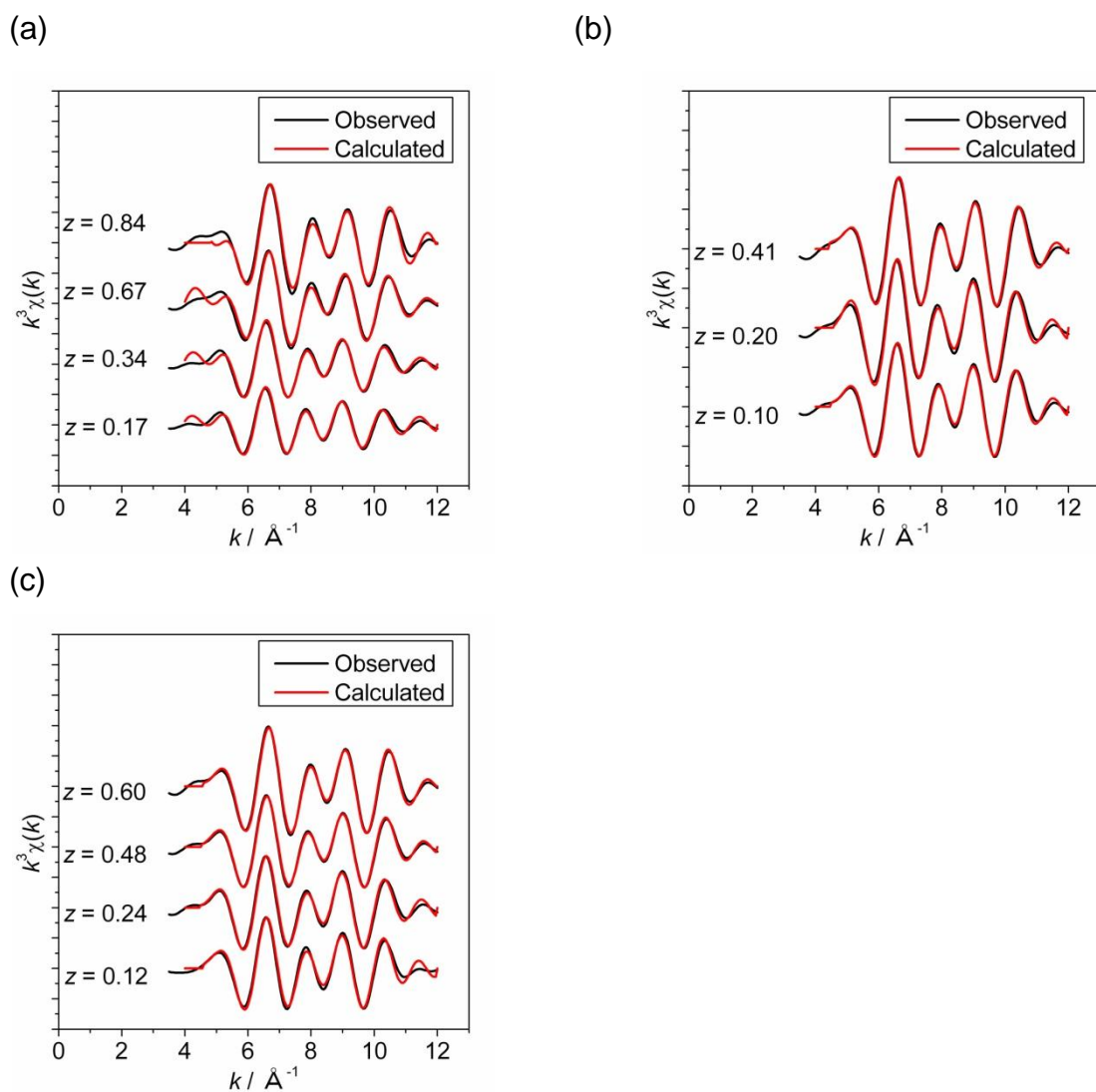


Figure S3 Curve-fitting results for inverse FT Mn K-edge EXAFS spectra of $\text{Li}_{1-z}\text{Mn}_2\text{O}_4$ (a), $\text{Li}_{1-z}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_4$ (b) and $\text{Li}_{1-z}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.964}\text{F}_{0.036}$ (c).

Table S1 Calculated parameters estimated from Mn K-edge EXAFS spectra for $\text{LiMn}_{2-x}\text{Li}_x\text{O}_4$ ($x = 0, 0.05, 0.10, 0.15$) (a), $\text{LiMn}_{1.9-y}\text{Li}_{0.1}\text{Ni}_y\text{O}_4$ ($y = 0.05, 0.10, 0.15, 0.20$) (b), $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-\eta}\text{F}_\eta$ ($\eta = 0, 0.036, 0.073$) (d), and Ni K-edge EXAFS spectra of $\text{LiMn}_{1.9-y}\text{Li}_{0.1}\text{Ni}_y\text{O}_4$ ($y = 0.10, 0.15, 0.20$) (c): interatomic distance (R) and Debye Waller factor (σ). Coordination number (CN) was fixed at fitting

(a)

x in $\text{LiMn}_{2-x}\text{Li}_x\text{O}_4$	Mn-O			Mn-M			Residue ^b / %
	CN^a	$R /$	$\sigma /$	CN^a	$R /$	$\sigma /$	
0	6	1.926(8)	0.087(13)	6	2.926(5)	0.066(8)	3.493
0.05	6	1.919(9)	0.086(12)	6	2.918(5)	0.068(8)	2.672
0.1	6	1.917(9)	0.083(13)	6	2.915(5)	0.066(8)	4.562
0.15	6	1.915(8)	0.079(12)	6	2.911(5)	0.068(8)	1.986

^a Fixed parameter for the curve-fitting procedure. ^b Residue = $100\{\sum\{k^3\chi_{\text{obs}}(k)-k^3\chi_{\text{calc}}(k)\}^2\}/\sum\{k^3\chi_{\text{obs}}(k)\}^2$.

(b)

y in $\text{LiMn}_{1.9-y}\text{Li}_{0.1}\text{Ni}_y\text{O}_4$	Mn-O			Mn-M			Residue ^b / %
	CN^a	$R /$	$\sigma /$	CN^a	$R /$	$\sigma /$	
0.05	6	1.915(9)	0.083(13)	6	2.913(5)	0.063(8)	3.852
0.1	6	1.913(8)	0.080(13)	6	2.911(5)	0.060(9)	4.398
0.15	6	1.911(9)	0.079(13)	6	2.908(5)	0.057(9)	4.836
0.2	6	1.910(9)	0.075(13)	6	2.907(5)	0.055(9)	4.392

^a Fixed parameter for the curve-fitting procedure. ^b Residue = $100\{\sum\{k^3\chi_{\text{obs}}(k)-k^3\chi_{\text{calc}}(k)\}^2\}/\sum\{k^3\chi_{\text{obs}}(k)\}^2$.

(c)

y in $\text{LiMn}_{1.9-y}\text{Li}_{0.1}\text{Ni}_y\text{O}_4$	Ni-O			Ni-M			Residue ^b / %
	CN^a	$R /$	$\sigma /$	CN^a	$R /$	$\sigma /$	
0.1	6	2.064(10)	0.067(19)	6	2.928(6)	0.058(11)	1.930
0.15	6	2.064(11)	0.067(19)	6	2.928(6)	0.058(11)	2.104
0.2	6	2.064(10)	0.067(19)	6	2.928(6)	0.058(11)	1.691

^a Fixed parameter for the curve-fitting procedure. ^b Residue = $100\{\sum\{k^3\chi_{\text{obs}}(k)-k^3\chi_{\text{calc}}(k)\}^2\}/\sum\{k^3\chi_{\text{obs}}(k)\}^2$.

(d)

η in $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-\eta}\text{F}_\eta$	Mn-O			Mn-M			Residue ^b / %
	CN^a	$R /$	$\sigma /$	CN^a	$R /$	$\sigma /$	
0	6	1.908(8)	0.082(12)	6	2.903(5)	0.069(8)	2.020
0.036	6	1.910(9)	0.086(12)	6	2.905(5)	0.072(8)	1.906
0.073	6	1.912(8)	0.088(12)	6	2.907(5)	0.075(8)	2.830

^a Fixed parameter for the curve-fitting procedure. ^b Residue = $100\{\sum\{k^3\chi_{\text{obs}}(k)-k^3\chi_{\text{calc}}(k)\}^2\}/\sum\{k^3\chi_{\text{obs}}(k)\}^2$.

Table S2 Calculated parameters estimated from Mn K-edge EXAFS spectra for $\text{Li}_{1-z}\text{Mn}_2\text{O}_4$ (a), $\text{Li}_{1-z}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_4$ (b) and $\text{Li}_{1-z}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.964}\text{F}_{0.036}$ (c): interatomic distance (R) and Debye Waller factor (σ). Coordination number (CN) was fixed at fitting

(a)

z in $\text{Li}_{1-z}\text{Mn}_2\text{O}_4$	Mn-O			Mn-M			Residue ^b / %
	CN^a	$R /$	$\sigma /$	CN^a	$R /$	$\sigma /$	
0.17	6	1.932(11)	0.099(16)	6	2.922(6)	0.081(9)	4.200
0.34	6	1.930(9)	0.096(14)	6	2.919(6)	0.077(9)	4.331
0.67	6	1.923(8)	0.072(15)	6	2.889(6)	0.059(11)	4.119
0.84	6	1.914(9)	0.067(16)	6	2.874(6)	0.057(12)	3.928

^a Fixed parameter for the curve-fitting procedure. ^b Residue = $100\{\sum\{k^3\chi_{\text{obs}}(k)-k^3\chi_{\text{calc}}(k)\}^2\}/\sum\{k^3\chi_{\text{obs}}(k)\}^2$.

(b)

z in $\text{Li}_{1-z}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_4$	Mn-O			Mn-M			Residue ^b / %
	CN^a	$R /$	$\sigma /$	CN^a	$R /$	$\sigma /$	
0.10	6	1.924(9)	0.079(15)	6	2.918(6)	0.061(11)	1.463
0.20	6	1.918(9)	0.076(15)	6	2.915(6)	0.060(11)	2.415
0.41	6	1.904(9)	0.070(15)	6	2.906(6)	0.057(11)	1.336

^a Fixed parameter for the curve-fitting procedure. ^b Residue = $100\{\sum\{k^3\chi_{\text{obs}}(k)-k^3\chi_{\text{calc}}(k)\}^2\}/\sum\{k^3\chi_{\text{obs}}(k)\}^2$.

(c)

z in $\text{Li}_{1-z}\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{3.964}\text{F}_{0.036}$	Mn-O			Mn-M			Residue ^b / %
	CN^a	$R /$	$\sigma /$	CN^a	$R /$	$\sigma /$	
0.12	6	1.921(10)	0.077(15)	6	2.921(6)	0.063(11)	3.290
0.24	6	1.919(9)	0.075(15)	6	2.919(6)	0.061(11)	1.881
0.48	6	1.915(9)	0.070(15)	6	2.900(6)	0.058(12)	0.652
0.60	6	1.911(9)	0.067(16)	6	2.886(6)	0.053(12)	0.950

^a Fixed parameter for the curve-fitting procedure. ^b Residue = $100\{\sum\{k^3\chi_{\text{obs}}(k)-k^3\chi_{\text{calc}}(k)\}^2\}/\sum\{k^3\chi_{\text{obs}}(k)\}^2$.