CHEMELECTROCHEM

Supporting Information

Synthesis and Electrochemistry of $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ Solid Solutions for Na-Ion Batteries

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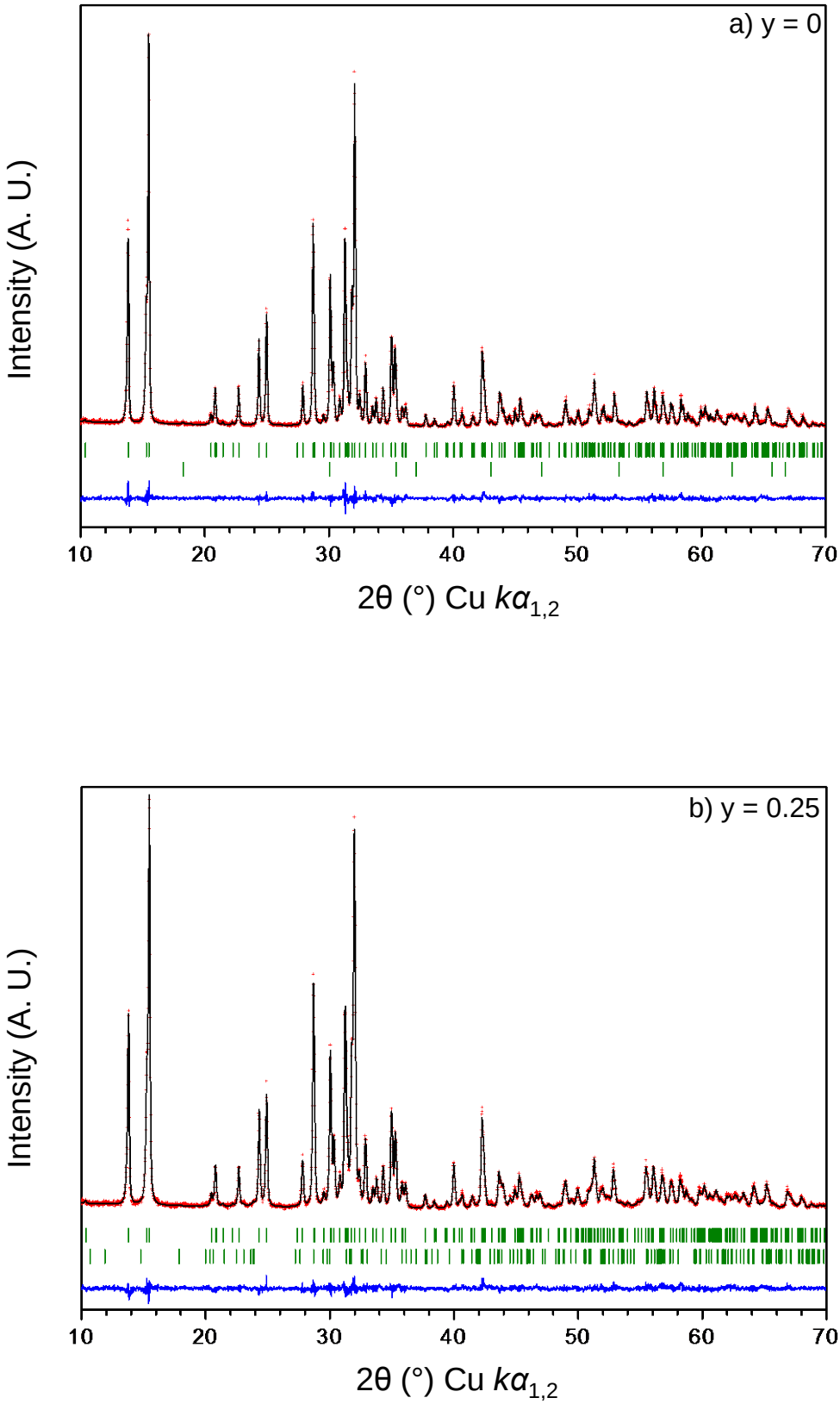

Figure S1. Observed and calculated (Rietveld method) of the a) $y = 0$, b) $y = 0.25$, c) $y = 0.5$, d) $y = 0.75$ and e) $y = 1$ $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ solid solutions. Red crosses: experimental, black line: calculated, blue line: difference and green bars: Bragg positions of the alluaudite (upper) and impurities (lower) phases.

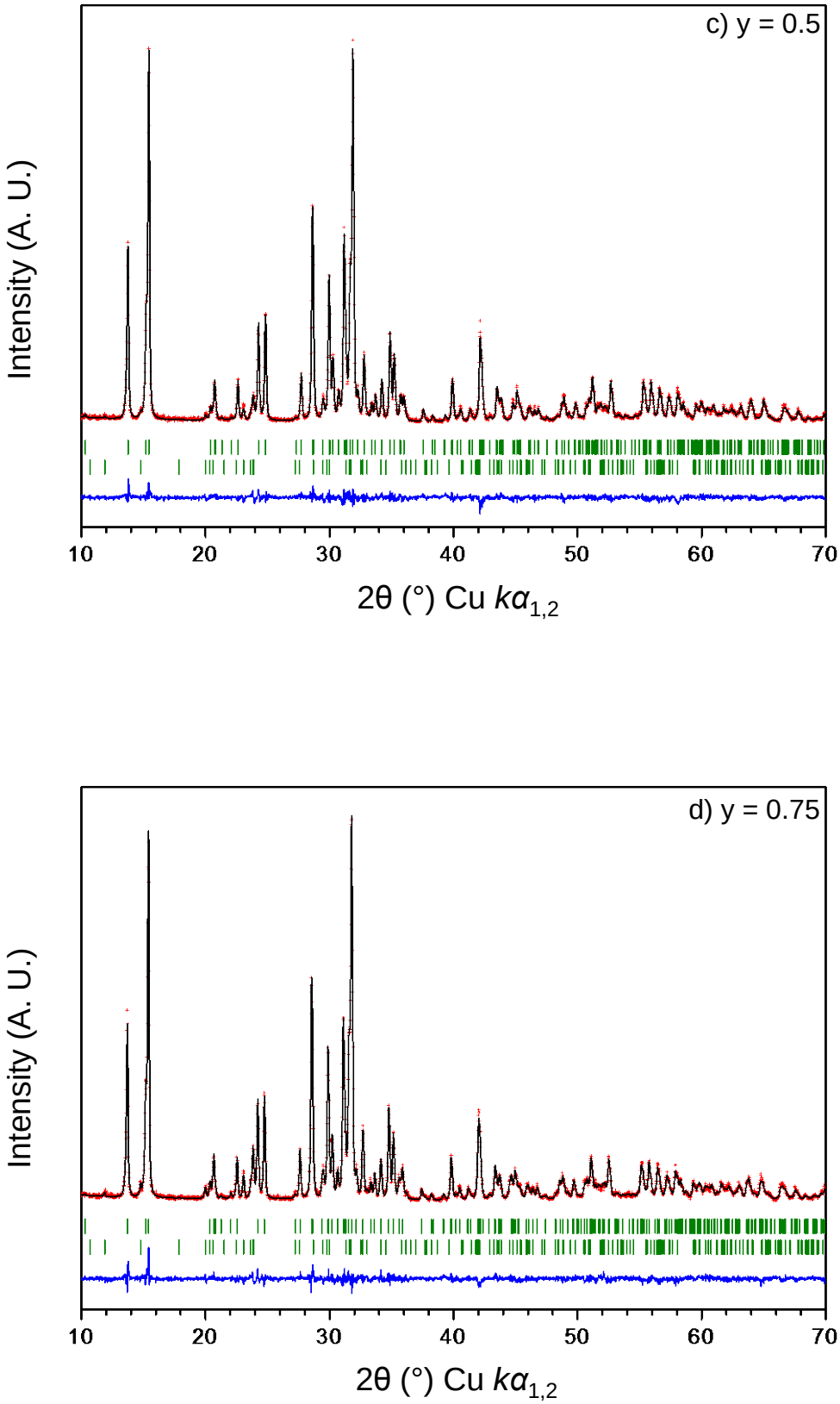

Figure S1. Observed and calculated (Rietveld method) of the a) $y = 0$, b) $y = 0.25$, c) $y = 0.5$, d) $y = 0.75$ and e) $y = 1$ $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ solid solutions. Red crosses: experimental, black line: calculated, blue line: difference and green bars: Bragg positions of the alluaudite (upper) and impurities (lower) phases.

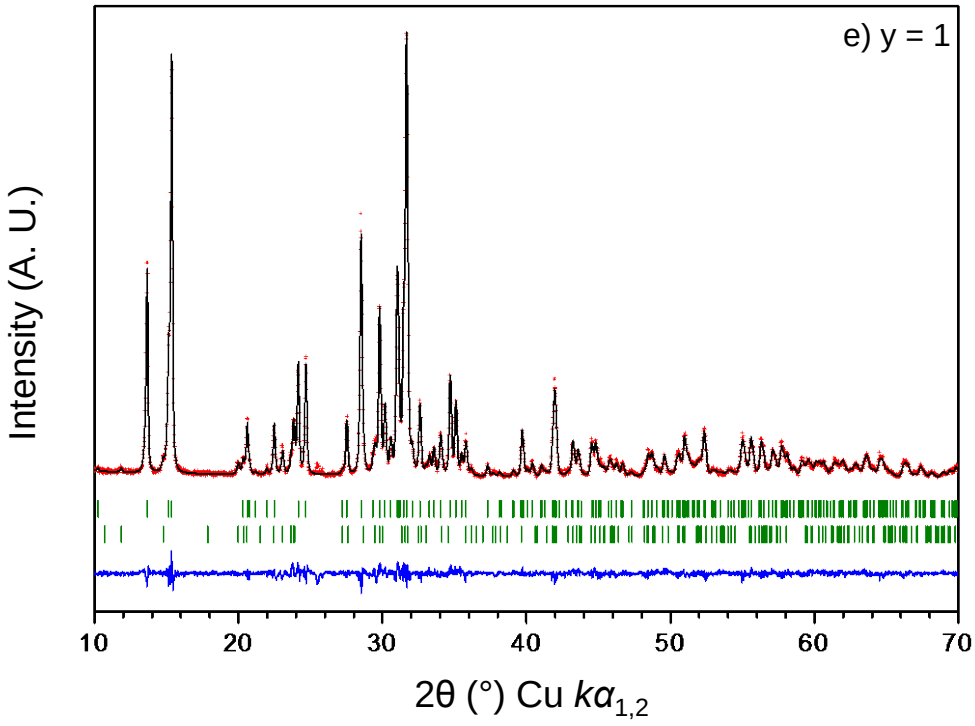

Figure S1. Observed and calculated (Rietveld method) of the a) *y* = 0, b) *y* = 0.25, c) *y* = 0.5, d) *y* = 0.75 and e) *y* = 1 $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ solid solutions. Red crosses: experimental, black line: calculated, blue line: difference and green bars: Bragg positions of the alluaudite (upper) and impurities (lower) phases.

a) $Na_{2.5}Fe_{1.75}(SO_4)_3$ (y = 0)

Space group: *C*2/*c*

a = 12.6603(3) Å, *b* = 12.7784(3) Å, *c* = 6.5179(1) Å, *β* = 115.55(1) °

V = 951.37(4) Å^3

% $Na_{2.5}Fe_{1.75}(SO_4)_3$ = 98.7 %, **% Fe_3O_4 =** 1.3 %

Reliability factors: R_{wp} = 8.5 %**, R_B =** 1.73 %

Atom	Site	Fractional coordinates			Occupancy	ADP (Å^2)
Na1	4*e*	0	0.7326(5)	1/4	1	2.2
Na2	4*a*	0	1/2	0	0.712(8)	5.8
Na3	4*e*	0	0.016(1)	1/4	0.57(2)	4
Na4	8*f*	0.2693(2)	0.3421(2)	0.3518(4)	0.140(5)	1.2
Fe	8*f*				0.854(4)	
S1	4*e*	0	0.2764(4)	1/4	1	1.2
O11	8*f*	0.0852(6)	0.3468(5)	0.214(1)	1	1.7
O12	8*f*	0.0544(5)	0.2085(5)	0.451(1)	1	1.5
S2	8*f*	0.2381(3)	0.1025(3)	0.1299(7)	1	1.4
O21	8*f*	0.2352(5)	0.1683(5)	0.317(1)	1	1
O22	8*f*	0.1782(5)	0.0032(6)	0.123(1)	1	2.2
O23	8*f*	0.3509(7)	0.0856(5)	0.165(1)	1	2.6
O24	8*f*	0.3256(5)	0.3407(5)	0.084(1)	1	1.7

Table S1. Structural and atomic parameters and reliability factors calculated from the Rietveld refinements of the structures based on the XRD patterns. a) *y* = 0, b) *y* = 0.25, c) *y* = 0.5, d) *y* = 0.75 and e) *y* = 1 $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ solid solutions. ADP values were fixed from those obtained from synchrotron XRD data in our previous work (ref. 9c in main text, G. Oyama et *al.,* Chem. ElectroChem., 2015).

b) $Na_{2.5}Fe_{1.31}Mn_{0.44}(SO_4)_3$ (y = 0.25)

Space group: *C*2/*c*

a = 12.6911(4) Å, *b* = 12.8213(4) Å, *c* = 6.5290(2) Å, *β* = 115.61(1) °

V = 958.00(5)

% $Na_{2.5}Fe_{1.31}Mn_{0.44}(SO_4)_3$ = 99.2 %, **% $Na_2Mn_3(SO_4)_4$ =** 0.8 %

Reliability factors: R_{wp} = 8.2 %**, R_B =** 1.8 %

Atom	Site	Fractional coordinates			Occupancy	ADP (Å²)
Na1	4*e*	0	0.7338(5)	1/4	1	2.2
Na2	4*a*	0	1/2	0	0.70(1)	5.8
Na3	4*e*	0	0.015(1)	1/4	0.55(1)	4
Na4	8*f*	0.2696(2)	0.3439(2)	0.3513(4)	0.125	1.2
Fe/Mn	8*f*				0.875	
S1	4*e*	0	0.2768(4)	1/4	1	1.2
O11	8*f*	0.0830(5)	0.3486(5)	0.212(1)	1	1.7
O12	8*f*	0.0551(5)	0.2103(5)	0.455(1)	1	1.5
S2	8*f*	0.2390(3)	0.1023(3)	0.1312(7)	1	1.4
O21	8*f*	0.2331(5)	0.1685(5)	0.316(1)	1	1
O22	8*f*	0.1767(5)	0.0051(6)	0.125(1)	1	2.2
O23	8*f*	0.3626(7)	0.0851(5)	0.167(1)	1	2.6
O24	8*f*	0.3270(6)	0.3396(5)	0.080(1)	1	1.7

Table S1. Structural and atomic parameters and reliability factors calculated from the Rietveld refinements of the structures based on the XRD patterns. a) $y = 0$, b) $y = 0.25$, c) $y = 0.5$, d) $y = 0.75$ and e) $y = 1$ $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ solid solutions. ADP values were fixed from those obtained from synchrotron XRD data in our previous work (ref. 9c in main text, G. Oyama et *al.,* Chem. ElectroChem., 2015).

c) $Na_{2.5}Fe_{0.875}Mn_{0.875}(SO_4)_3$ (y = 0.5)

Space group: *C*2/*c*

a = 12.7227(4) Å, b = 12.8656(4) Å, c = 6.5452(2) Å, β = 115.66(1) °

V = 965.69(5) Å^3

% $Na_{2.5}Fe_{0.875}Mn_{0.875}(SO_4)_3$ = 95.4 %, **% $Na_2Mn_3(SO_4)_4$ =** 4.6 %

Reliability factors: R_{wp} = 8.5 %**, R_B =** 2.3 %

Atom	Site	Fractional coordinates			Occupancy	ADP (Å^2)
Na1	4*e*	0	0.7331(6)	1/4	1	2.2
Na2	4*a*	0	1/2	0	0.71(1)	5.8
Na3	4*e*	0	0.015(1)	1/4	0.54(1)	4
Na4	8*f*	0.2700(2)	0.3450(2)	0.3406(4)	0.125	1.2
Fe/Mn	8*f*				0.875	
S1	4*e*	0	0.2770(4)	1/4	1	1.2
O11	8*f*	0.0823(6)	0.3492(5)	0.210(1)	1	1.7
O12	8*f*	0.0556(6)	0.2117(5)	0.456(1)	1	1.5
S2	8*f*	0.2387(4)	0.1030(3)	0.1308(7)	1	1.4
O21	8*f*	0.2332(6)	0.1677(5)	0.317(1)	1	1
O22	8*f*	0.1741(5)	0.0050(7)	0.123(1)	1	2.2
O23	8*f*	0.3639(7)	0.0860(5)	0.171(1)	1	2.6
O24	8*f*	0.3270(6)	0.3403(5)	0.077(1)	1	1.7

Table S1. Structural and atomic parameters and reliability factors calculated from the Rietveld refinements of the structures based on the XRD patterns. a) y = 0, b) y = 0.25, c) y = 0.5, d) y = 0.75 and e) y = 1 $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ solid solutions. ADP values were fixed from those obtained from synchrotron XRD data in our previous work (ref. 9c in main text, G. Oyama et *al.,* Chem ElectroChem., 2015).

d) $Na_{2.5}Fe_{0.44}Mn_{1.31}(SO_4)_3$ (y = 0.75)

Space group: *C*2/*c*

a = 12.7566(4) Å, *b* = 12.9095(4) Å, *c* = 6.5605(2) Å, *β* = 115.72(1) °

V = 973.37(5) Å^3

% $Na_{2.5}Fe_{0.44}Mn_{1.31}(SO_4)_3$ = 91.8 %, **% $Na_2Mn_3(SO_4)_4$ =** 8.2 %

Reliability factors: R_{wp} = 8.8 %**, R_B =** 2.2 %

Atom	Site	Fractional coordinates			Occupancy	ADP (Å^2)
Na1	4*e*	0	0.7313(6)	1/4	1	2.2
Na2	4*a*	0	1/2	0	0.67(1)	5.8
Na3	4*e*	0	0.016(1)	1/4	0.58(1)	4
Na4	8*f*	0.2700(2)	0.3457(2)	0.3511(4)	0.125	1.2
Fe/Mn	8*f*				0.875	
S1	4*e*	0	0.2796(4)	1/4	1	1.2
O11	8*f*	0.0836(6)	0.3503(6)	0.213(1)	1	1.7
O12	8*f*	0.0552(6)	0.2139(5)	0.454(1)	1	1.5
S2	8*f*	0.2375(1)	0.1027(3)	0.1298(8)	1	1.4
O21	8*f*	0.2332(6)	0.1687(6)	0.314(1)	1	1
O22	8*f*	0.1744(6)	0.0050(7)	0.121(1)	1	2.2
O23	8*f*	0.3626(8)	0.0877(6)	0.171(1)	1	2.6
O24	8*f*	0.3297(6)	0.3398(6)	0.083(1)	1	1.7

Table S1. Structural and atomic parameters and reliability factors calculated from the Rietveld refinements of the structures based on the XRD patterns. a) $y = 0$, b) $y = 0.25$, c) $y = 0.5$, d) $y = 0.75$ and e) $y = 1$ $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ solid solutions. ADP values were fixed from those obtained from synchrotron XRD data in our previous work (ref. 9c in main text, G. Oyama et *al.,* Chem ElectroChem., 2015).

e) $Na_{2.6}Mn_{1.7}(SO_4)_3$ (y = 1.0)

Space group: *C*2/*c*

a = 12.7931(4) Å, *b* = 12.9511(4) Å, *c* = 6.5724(2) Å, *β* = 115.77(1) °

V = 980.67(6) Å^3

% $Na_{2.6}Mn_{1.7}(SO_4)_3$ = 91.7 %, **% $Na_2Mn_3(SO_4)_4$ =** 8.3 %

Reliability factors: R_{wp} = 8.9 %**, R_B =** 2.3 %

Atom	Site	Fractional coordinates			Occupancy	ADP (Å^2)
Na1	4*e*	0	0.7330(7)	1/4	1	2.2
Na2	4*a*	0	1/2	0	0.72(1)	5.8
Na3	4*e*	0	0.020(1)	1/4	0.56(1)	4
Na4	8*f*	0.2708(3)	0.3460(2)	0.3523(5)	0.13(2)	1.2
Mn	8*f*				0.86(1)	
S1	4*e*	0	0.2801(5)	1/4	1	1.2
O11	8*f*	0.0853(7)	0.3496(6)	0.219(1)	1	1.7
O12	8*f*	0.0547(7)	0.2147(6)	0.453(2)	1	1.5
S2	8*f*	0.2368(4)	0.1042(3)	0.1313(8)	1	1.4
O21	8*f*	0.2337(6)	0.1703(6)	0.319(1)	1	1
O22	8*f*	0.1765(6)	0.0075(7)	0.1222(1)	1	2.2
O23	8*f*	0.3595(8)	0.0895(6)	0.170(1)	1	2.6
O24	8*f*	0.3267(7)	0.3402(6)	0.087(1)	1	1.7

Table S1. Structural and atomic parameters and reliability factors calculated from the Rietveld refinements of the structures based on the XRD patterns. a) $y = 0$, b) $y = 0.25$, c) $y = 0.5$, d) $y = 0.75$ and e) $y = 1$ $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ solid solutions. ADP values were fixed from those obtained from synchrotron XRD data in our previous work (ref. 9c in main text, G. Oyama et *al.,* Chem ElectroChem., 2015).

Pristine materials					
Site	**Parameters**	***y* = 0**	***y* = 0.25**	***y* = 0.5**	***y* = 0.75**
Fe^{2+}	**δ (mms^{-1})**	1.280(1)	1.281(2)	1.278(2)	1.277(1)
	Δ* (mms^{-1})	2.20(1)	2.21(1)	2.31(1)	2.33(1)
	Pop. (%)	100	100	100	100
After charge to 4.4 V					
Site	**Parameters**	***y* = 0**	***y* = 0.25**	***y* = 0.5**	***y* = 0.75**
Fe^{2+}	**δ (mms^{-1})**	1.224(1)	1.24(1)	1.26(4)	1.283(5)
	Δ* (mms^{-1})	2.60(1)	2.54(1)	2.35(1)	2.36(1)
	Pop. (%)	12	23	33	84
Fe^{3+}	**δ (mms^{-1})**	0.484(1)	0.487(4)	0.485(4)	0.55(2)
	Δ* (mms^{-1})	0.86(1)	0.83(1)	0.73(1)	0.35(4)
	Pop. (%)	88	77	67	16
After discharge back to 2.5 V					
Site	**Parameters**	***y* = 0**	***y* = 0.25**	***y* = 0.5**	***y* = 0.75**
Fe^{2+}	**δ (mms^{-1})**	1.277(2)	1.281(1)	1.275(1)	1.286(3)
	Δ* (mms^{-1})	2.0(1)	2.11(4)	2.25(1)	2.34(1)
	Pop. (%)	100	100	100	100

Table S2. Mossbauer parameters (isomer shift (δ), quadrupole splitting (Δ*) and population (Pop.) of of the $Na_{2.5}(Fe_{1-y}Mn_y)_{1.75}(SO_4)_3$ solid solutions (y = 0, 0.25, 0.5 and 0.75) in their pristine, charged (4.4 V) and discharged (2.5 V) states.