Supporting Information

Activation of anion redox in P3 structure cobalt-doped sodium manganese oxide via introduction of transition metal vacancies

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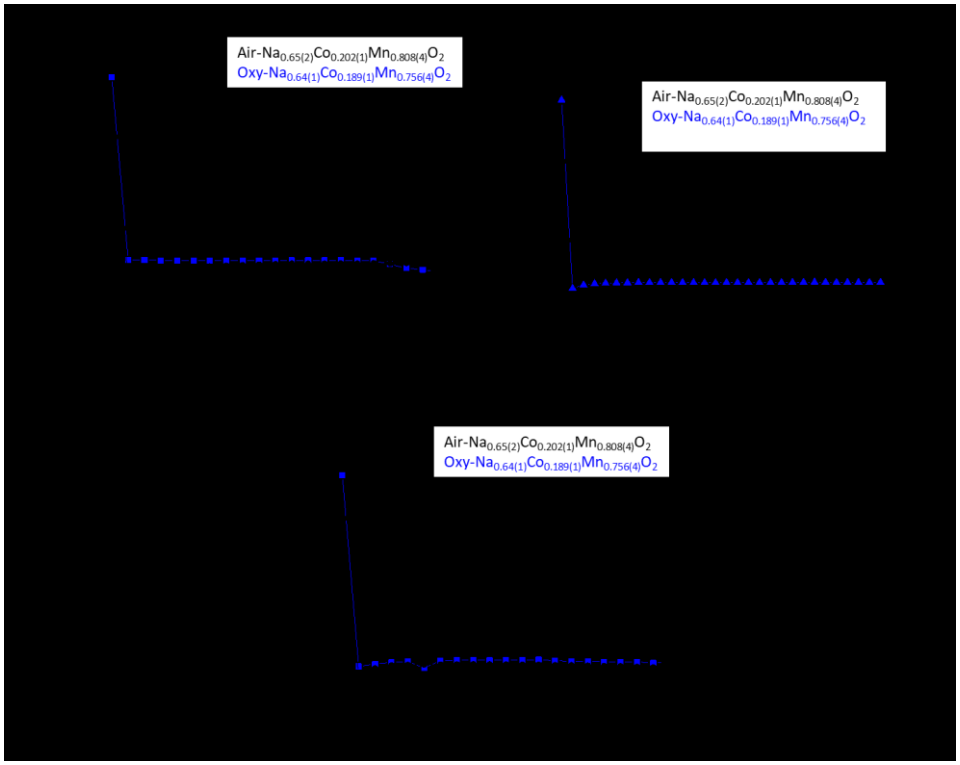

Figure S1. Coulombic efficiency of Air-$Na_{0.65(2)}Co_{0.202(1)}Mn_{0.808(4)}O_2$ (black) and Oxy-$Na_{0.64(1)}Co_{0.189(1)}Mn_{0.756(4)}O_2$ (blue) cycled at 30 °C in the voltage ranges of 1.8–3.8 V at a rate of (a) 10 mA g^{-1}, (b) 100 mA g^{-1} and (c) in the voltage ranges of 1.8–4.4 V at a rate of 10 mA g^{-1}.

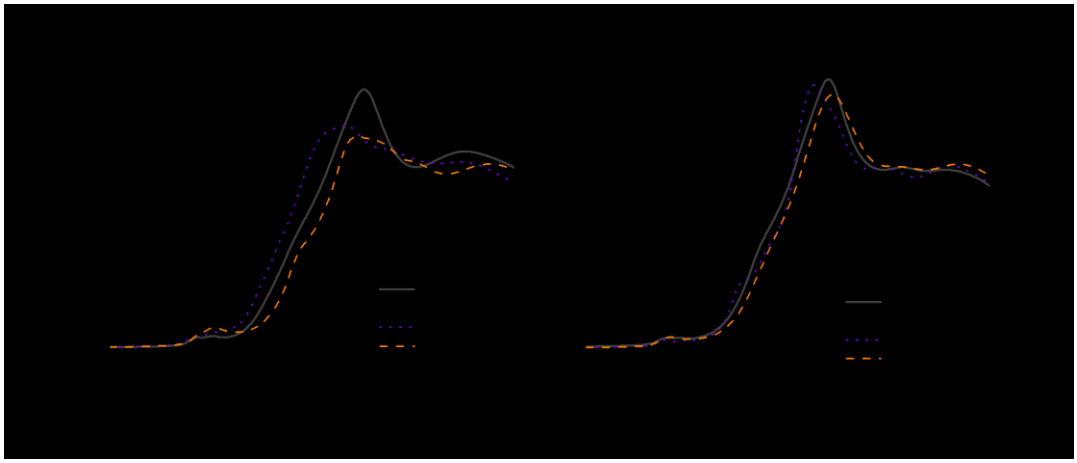

Figure S2. (a) Mn K-edge XANES spectra compared with reference of Mn^{3+} (Mn_2O_3) and Mn^{4+} (MnO_2) and (b) Co K-edge XANES spectra compared with reference of Co^{3+} ($LiCoO_2$) and Co^{4+} ($LiCoO_2$ charged to 4.7 V) of the pristine Air-$Na_{0.65(2)}Co_{0.202(1)}Mn_{0.808(4)}O_2$ (grey) and Oxy-$Na_{0.64(1)}Co_{0.189(1)}Mn_{0.756(4)}O_2$ (black).

Table S1. Rietveld refinement results of (a) Air-$Na_{0.65(2)}Co_{0.202(1)}Mn_{0.808(4)}O_2$ charged to 4.4 V, (b) Oxy-$Na_{0.64(1)}Co_{0.189(1)}Mn_{0.756(4)}O_2$ charged to 4.4 V, (c) Air-$Na_{0.65(2)}Co_{0.202(1)}Mn_{0.808(4)}O_2$ and discharged to 1.8 V, (d Oxy-$Na_{0.64(1)}Co_{0.189(1)}Mn_{0.756(4)}O_2$ charged to 4.4 V and discharged to 1.8 V.

(a) Air-$Na_{0.65(2)}Co_{0.202(1)}Mn_{0.808(4)}O_2$ charged to 4.4 V						
R_{exp} = 2.02% R_{wp} = 2.66% 94(2)% P3, 6(2)% O3 Lattice parameters P3 Space group *R3m* *a* = *b* = 2.8340(7) *c* = 16.865(5) Å						
atom	Wyckoff symbol	x/a	y/b	z/c	Occupancy	Biso
Co1/Mn1	3a	0	0	0	0.2/0.8	0.3
Na1	3a	0	0	0.1601(12)	0.42(1)	1.2
O1	3a	0	0	0.3807(8)	1	0.5
O2	3a	0	0	0.5959(10)	1	0.5
Lattice parameters O3 Space group *R-3m* *a* = *b* = 2.833(3) *c* = 14.095(11) Å						
Co1/Mn1	3a	0	0	0	0.2/0.8	0.3
Na1	3b	0	0	0.5	0.20(5)	1.2
O1	6c	0	0	0.266(1)	1	0.5

(b) Oxy-$Na_{0.64(1)}Co_{0.189(1)}Mn_{0.756(4)}O_2$ charged to 4.4 V						
R_{exp} = 2.09% R_{wp} = 2.83% Lattice parameters P3 Space group *R3m* *a* =2.8321(7) *c* = 16.884(8) Å						
atom	Wyckoff symbol	x/a	y/b	z/c	Occupancy	Biso
Co1/Mn1	3a	0	0	0	0.19/0.76	0.3
Na1	3a	0	0	0.1625(6)	0.42(1)	1.2
O1	3a	0	0	0.3853(7)	1	0.5
O2	3a	0	0	0.5990(7)	1	0.5

(c) Air-$Na_{0.65(2)}Co_{0.202(1)}Mn_{0.808(4)}O_2$ charged to 4.4 V and discharged to 1.8 V						
R_{exp} = 2.12% R_{wp} = 2.33% 81(2)% O'3, 19(2)% P3 Lattice parameters O'3 Space group *C2/m* a =5.432(2) Å b = 2.8911(7) Å c = 5.7413(16) Å β = 111.10(2)°						
atom	Wyckoff symbol	x/a	y/b	z/c	Occupancy	Biso
Co1/Mn1	2a	0	0	0	0.2/0.8	0.3
Na1	2d	0	0.5	0.5	0.952(7)	1.2
O1	4i	0.262(2)	0	0.792(2)	1	0.5
Lattice parameters P3 Space group *R3m* a = b = 2.852(4) c = 16.608(5) Å						
Co1/Mn1	3a	0	0	0	0.2/0.8	0.5
Na1	3a	0	0	0.175(2)	0.86(5)	1.2
O1	3a	0	0	0.403(4)	1	0.5
O2	3a	0	0	0.598(5)	1	0.5

(d) Oxy-$Na_{0.64(1)}Co_{0.189(1)}Mn_{0.756(4)}O_2$ charged to 4.4 V and discharged to 1.8 V						
R_{exp} = 2.15% R_{wp} = 2.87% 83(2)% O'3, 17(2)% P3 Lattice parameters O'3 Space group *C2/m* a =5.358(2) Å b = 2.9180(6) Å c = 5.7133(13) Å β = 110.13(2)°						
atom	Wyckoff symbol	x/a	y/b	z/c	Occupancy	Biso
Co1/Mn1	2a	0	0	0	0.19/0.76	0.3
Na1	2d	0	0.5	0.5	0.943(9)	1.2
O1	4i	0.265(2)	0	0.808(2)	1	0.5
Lattice parameters P3 Space group *R3m* a = b = 2.8607(10) c = 16.639(6) Å						
Co1/Mn1	3a	0	0	0	0.19/0.76	0.3
Na1	3a	0	0	0.170(2)	0.88(6)	1.2
O1	3a	0	0	0.386(5)	1	0.5
O2	3a	0	0	0.615(5)	1	0.5