Electronic Supporting Information

for

Influence of Manganese and Cobalt content on the electrochemical performances of P2-Na_{0.67}Mn_xCo_{1-x}O₂ cathodes for sodium ion batteries

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S1. X-ray diffraction data of (1) $Na_{0.67}Mn_{0.25}Co_{0.75}O_2$ (2) $Na_{0.67}Mn_{0.5}Co_{0.5}O_2$ (3) $Na_{0.67}Mn_{0.75}Co_{0.25}O_2$. The data shows the shift of base peak towards right as the cobalt content is increased indicating decrease in cell volume.



S2. Crystallographic parameters of P2- $Na_{0.67}Mn_xCo_{1-x}O_2$ (x = 0.75, 0.5, 0.25) derived from Rietveld refinement of X-ray diffraction data. Cobalt doped $Na_{0.67}MnO_2$ phases were refined with hexagonal P6₃/mmc and for $Na_{0.67}MnO_2$ phase, better convergence was achieved with orthorhombic, *Cmcm*, system. With increase in cobalt content, shortening of lattice parameters '*a*' and '*c*' and contraction of MO_6 octahedra is observed which offers more inter-layer space for Na-ion transport.

Cell parameters	Na _{0.67} Mn _{0.75} Co _{0.25} O ₂	Na _{0.67} Mn _{0.5} Co _{0.5} O ₂	Na _{0.67} Mn _{0.25} Co _{0.75} O ₂	Na _{0.67} MnO ₂
a = b(A) $c(A)$	2.8694 (4) 11.2637(3)	2.8267(4) 11.2293(3)	2.8305(4) 11.0134(3)	$a(\hat{A})=2.8518(3)$ $b(\hat{A})=5.109(4)$ $c(\hat{A})=11.133(3)$
Cell volume(Å ³)	80.310	77.700	76.410	162.21
Na1–O1 bond(Å)	2.559 2.539 2.512		2.512	2.355
O1-Na2-O1 bond (Å)	3.9012	3.8894	3.8146	-
Co/Mn-O bond (Å)	1.8689(4) x 2 1.8691(5) x 4	1.8458 (5) x 2 1.8460 (4) x 4	1.8400 (6) x 2 1.8403 (4) x 4	1.7562 (4) x 4 2.3136 (5) x 2

	3.8146	3.8894	3.9013	-
NaO2 layer height (Å)				

S3.Rietveld fit of $Na_{0.67}MnO_2$ sample and table of refined crystallographic parameters. Better convergence was obtained for orthorhombic *Cmcm* model system indicating strong Jahn-Teller distortion.¹



Lattice parameters : $a(\hat{A})=2.8519(3)$, $b(\hat{A})=5.1090(4)$, $c(\hat{A}) = 11.1328(3)$, Space group : *Cmcm* (No.63), $R_{exp} = 7.1$. χ^2 (G²) = 4.1. M–O bond lengths (Å): 1.7562(4) x 4, 2.3136(5) x 2. S4. (a) Surface morphology of (1) $Na_{0.67}Mn_{0.25}Co_{0.75}O_2$ and (2) $Na_{0.67}Mn_{0.75}Co_{0.25}O_2$, corresponding (b) EDS profile and Elemental mapping showing distribution of (d) sodium (e) cobalt (f) manganese and (g) oxygen for the image shown as inset (c). Flaky polyhedral shaped particles with homogenous distribution of all elements are observed.





S5: X-ray photoelectron spectroscopy analysis of Na_{0.67}Mn_xCo_{1-x}O₂ (x=0.25, 0.5, 0.75) phases. Survey spectra (A), C1s (B), Na 1s (C) and O 1s (D) are presented here. XPS survey spectrum of Na_{0.67}Mn_xCo_{1-x}O₂ shows peaks corresponding to Na, Mn, Co, O and C at 1071, 641, 779, 530 and 285 eV, respectively. Adventitious C 1s was observed at 284.5 eV and all binding energies could be referenced to this value.² Deconvoluted C 1s spectrum is composed of three peaks. The sharp and large peak observed at 284.5 eV corresponds to adventitious carbon.² The peaks at 285.7 and 288.6 eV could be attributed to the defect containing carbon and carboxyl (–C=O) carbons, respectively.² O1s spectrum shows strong influence of composition on XPS data and is composed of three individual peaks around 529.6, 530.6 and 532.6 eV. The first peak at 529.6 eV corresponds to O_2^{2-} anions in the crystal lattice.³ The peak at 531.0 eV may be due to the lattice oxygen with coordination deficiency.³ The weak peak at 532.6 eV is due to the surface adsorbed species.³ Na1s peak observed at 1071.2 eV is attributed to the Na⁺ species.²



S6: X-ray photoelectron spectroscopy analysis of $Na_{0.67}Mn_xCo_{1-x}O_2$ (x=0.25, 0.5, 0.75) phases. The oxidation states and the composition of manganese and cobalt species obtained from the XPS analysis are closer to their theoretical values.

Element		x = 0.75	x = 0.50	x = 0.25
		642.8	642.1	641.8
	Mn ⁴⁺	643.8	642.9	642.7
	FWHM = 1.2-	644.6	643.9	643.5
	1.25	645.6	644.8	644.3
Mn2p _{3/2}		646.7	645.8	645.3
eV		641.5	641.1	-
	Mn ³⁺ FWHM	642.2	641.7	-
	= 1.0- 1.1	643.0	642.5	-
		644.0	643.4	-
		645.4	644.4	-
		780.1	780.1	779.9
Co2p _{3/2}	C0 ³⁺	781.4	781.4	780.9
eV		783.2	783.2	782.2
		787.2 ^{sat}	789.2 sat	789.5 sat
	C0 ⁴⁺			785.2
Theoretical composition		Co ³⁺ = 100% Mn ³⁺ :Mn ⁴⁺ = 56: 44 %	Co ³⁺ = 100% Mn ³⁺ :Mn ⁴⁺ = 34: 66 %	Co ³⁺ :Co ⁴⁺ = 88 : 12 % Mn ⁴⁺ = 100 %
Composition from XPS data analysis		$\frac{\text{Co}^{3+} = 100\%}{\text{Mn}^{3+}:\text{Mn}^{4+} = 58:42\%}$	$\frac{\text{Co}^{3+} = 100\%}{\text{Mn}^{3+}:\text{Mn}^{4+} = 35:65\%}$	Co ³⁺ : Co ⁴⁺ = 90: 10 % Mn ⁴⁺ = 100%

S7: Oxygen estimation of $Na_{0.67}Mn_xCo_{1-x}O_2$ (x=0.25, 0.5, 0.75). Chemical estimation of oxygen content was carried out by iodometric titration.⁴ The nominal compositions, oxygen non-stoichiometric compositions derived from the estimation and the compositions with oxygen normalized are presented. The estimation indicated increase in oxygen non-stoichiometry with increase in cobalt content. In other words, increase in manganese concentration resulted in more oxygen uptake.

S No	Nominal composition	Oxygen non stoichiometric composition	Oxygen Normalised composition	Capacity from cycling (mAh g ⁻¹)
1	Na _{0.67} Mn _{0.75} Co _{0.25} O ₂	Na _{0.67} Mn _{0.75} Co _{0.25} O _{2.0225}	$Na_{0.6625}Mn^{3+}{}_{0.3708}Mn^{4+}{}_{0.3708}Co_{0.2472}O_2$	167
2	Na _{0.67} Mn _{0.50} Co _{0.50} O ₂	$Na_{0.67}Mn_{0.50}Co_{0.50}O_{1.95235}$	$Na_{0.6862}Mn^{3+}{}_{0.2716}Mn^{4+}{}_{0.2404}Co_{0.5122}O_2$	145
3	Na _{0.67} Mn _{0.25} Co _{0.75} O ₂	$Na_{0.67}Mn_{0.25}Co_{0.75}O_{1.8981}$	$Na_{0.705}Mn^{3+}{}_{0.1304}Mn^{4+}{}_{0.1329}Co_{0.7902}O_2$	120

S8: dQ/dV plots of Na_{0.67}Mn_xCo_{1-x}O₂ (x=0.25, 0.5, 0.75). The data indicate that all phases undergo reversible phase transitions from the second cycle onwards and the observed redox voltages closely mimic the cyclic voltammograms (**Fig. 5**, main article).



S9. Summary of literature on $Na_xMn_yCo_{1-y}O_2$ phases

Phase	1 st discharge capacity in mAhg ⁻¹ (C-rate (or) current density in mA/g)	Discharge capacity and retention (%)	Voltage range	Diffusion coefficient range	Reference
$\begin{array}{c} Na_{0.67}Mn_{0.17}Co_{0.83}O_2\\ Na_{0.67}Mn_{0.33}Co_{0.67}O_2\\ Na_{0.67}Mn_{0.5}Co_{0.5}O_2\\ Na_{0.67}Mn_{0.67}Co_{0.33}O_2\\ Na_{0.67}Mn_{0.83}Co_{0.17}O_2\\ \end{array}$	~100 ~118 123 ~140 ~150 (30mA/g)	~85 (85%) ~80 (68%) 85 (69%) ~100 (71%) ~82 (55%) (30 th cycle)	1.5 – 4 V	-	5
$\begin{array}{c} Na_{0.7}Mn_{0.2}Co_{0.8}O_2\\ Na_{0.7}Mn_{0.3}Co_{0.6}O_2\\ Na_{0.7}Mn_{0.6}Co_{0.4}O_2\\ \end{array}$	~84 ~87 ~70 (C/20) (2 nd discharge)	-	1.5 – 3.8 V	-	6
$\begin{array}{c} Na_{0.67}Mn_{0.25}Co_{0.75}O_2\\ Na_{0.67}Mn_{0.5}Co_{0.5}O_2\\ Na_{0.67}Mn_{0.75}Co_{0.25}O_2\\ \end{array}$	116 139 157 (0.1C=25mA/g)	107 (91%) 121 (87%) 126 (79%) (100 th cycle)	1.5 – 4.2 V	10 ⁻⁹ to 10 ⁻ 13	Present work
Na _{0.7} Mn _{0.89} Co _{0.11} O ₂	138 (0.3C)	92 (67%)	1.5 – 3.8 V	-	7
Na _{0.6} Mn _{0.9} Co _{0.1} O ₂	140 (50 mA/g)	~99 (71%) (100 th cycle)	1.5 – 3.8 V	-	8
Na _{0.67} Mn _{0.33} Co _{0.67} O ₂	~119 (C/100)	-	1.5 – 4.0 V	-	9
Na _{0.79} Mn _{0.3} Co _{0.7} O ₂	60 (C/2)	~53 (89%) (60 th cycle)	2.0 – 3.75 V	-	10
$\boxed{\begin{array}{c} Na_{0.4}Mn_{0.54}Co_{0.46}O_2\\ Na_{0.4}Mn_{0.4}Co_{0.6}O_2\end{array}}$	~175 ~130 (20mA/g)	~120 (71%) ~110 (84%) (70 th cycle)	1.5 – 4.2 V	-	11
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	140 120 120	~130 (93%) ~100 (83%) ~130	1.5 - 4.3 V	-	12

(1C)	(100 th cycle)		

S10. Cyclic voltammetry plot of (1) $Na_{0.67}Mn_{0.25}Co_{0.75}O_2$ (2) $Na_{0.67}Mn_{0.5}Co_{0.5}O_2$ and (3) $Na_{0.67}Mn_{0.75}Co_{0.25}O_2$ at different scan rates: 0.2, 0.4, 0.6, 0.8 and 1 mV/s. The cyclic voltammetric data is used to derive the sodium-ion diffusion coefficients using Equation 1 and 2. Linear fit of peak current versus square root of scan rate is presented in Fig. S11 and the calculated diffusion coefficients are presented in Table S13.

$$i_p = 2.69 \text{ X } 10^5 A n^{3/2} C D^{1/2} v^{1/2}$$
 ---- (1)

On rearranging eq. (1) and substituting slope (m) = $i_p/\upsilon^{1/2}$,

$$D = [\text{slope} (m)/(2.69 \text{ X } 10^5 A n^{3/2} C)]^2 \qquad \qquad \text{---} (2)$$



S11. Relationship of the peak current (i_p) as a function of square root of scan rate for (1) Na_{0.67}Mn_{0.25}Co_{0.75}O₂ (2) Na_{0.67}Mn_{0.5}Co_{0.5}O₂ (3) Na_{0.67}Mn_{0.75}Co_{0.25}O₂. From the slope of linear fit obtained, sodium ion diffusion coefficient is calculated using Equation 2 (Refer S10).



S12. Relationship between Z_{real} (Z') and the reciprocal of square root of angular frequency $(\omega^{-1/2})$ in the low frequency region corresponding to first (square in blue) and fifth discharge (circle in red) of (1) Na_{0.67}Mn_{0.25}Co_{0.75}O₂ (2) Na_{0.67}Mn_{0.5}Co_{0.5}O₂ (3) Na_{0.67}Mn_{0.75}Co_{0.25}O₂. The slope (σ) is obtained from the linear fit (shown in black) of Z_{real} and $\omega^{-1/2}$. From the slope, diffusion coefficients are calculated. The results at the end of 1st as well as 5th discharge (Table S13) showed enhancement in Na-ion transport with cobalt substitution.



S13. Sodium ion diffusion coefficients calculated from CV recorded at varying scan rates from 0.2 - 1.0 mV/s and EIS conducted at first and fifth discharge. From analysis of CV and EIS data, it is clear that cobalt substitution enhances Na-ion mass transport.

CV	Slope (m) Oxidation	D_{Na^+}	Slope (m) Reduction	$\mathbf{D}_{\mathbf{Na}^+}$		
1.	$Na_{0.67}Mn_{0.25}Co_{0.75}O_2$					
	0.03742	6.96 X 10 ⁻⁹	0.03298	5.41 X 10 ⁻⁹		
	0.04147	8.55 X 10 ⁻⁹	0.03336	5.53 X 10 ⁻⁹		
2.		Na _{0.67} Mn _{0.5}	C0 _{0.5} O ₂			
	0.03185	5.04 X 10 ⁻⁹	0.03216	5.14 X 10 ⁻⁹		
3.		Na _{0.67} Mn _{0.75}	Co _{0.25} O ₂			
	0.03414	4.42 X 10 ⁻⁹	0.03632	5.00 X 10 ⁻⁹		
EIS	Slope (σ) 1 st discharge	$D_{Na^{+}}$	Slope (σ) 5 th discharge	$\mathbf{D}_{\mathbf{Na}^{\star}}$		
1.	Na _{0.67} Mn _{0.25} Co _{0.75} O ₂					
	42.7983	1.68 X 10 ⁻¹¹	44.7006	1.54 X 10 ⁻¹¹		
2.	$Na_{0.67}Mn_{0.5}Co_{0.5}O_2$					
	129.2639	1.66 X 10 ⁻¹²	133.7141	1.55 X 10 ⁻¹²		
3.	Na _{0.67} Mn _{0.75} Co _{0.25} O ₂					
	240.5216	1.68 X 10 ⁻¹³	253.3889	1.52 X 10 ⁻¹³		

S14. Nyquist plot of (1) Na_{0.67}Mn_{0.25}Co_{0.75}O₂ (2) Na_{0.67}Mn_{0.5}Co_{0.5}O₂, 3) Na_{0.67}Mn_{0.75}Co_{0.25}O₂ at different peak potentials as observed in cyclic voltammogram carried out at 0.05mV/s scan rate (shown in main paper Fig.5). By plotting Z_{real} (Z') versus ($\omega^{-1/2}$) and using the slope obtained (Figure S13), diffusion coefficients are calculated according to Equations 3 and 4 and presented in Table S16.



S15. Relationship between Z_{real} and $\omega^{-1/2}$ in the low frequency region of (1) Na_{0.67}Mn_{0.25}Co_{0.75}O₂ (2) Na_{0.67}Mn_{0.5}Co_{0.5}O₂ (3) Na_{0.67}Mn_{0.75}Co_{0.25}O₂ for the impedance measured by stopping at different peak potentials as observed in cyclic voltammetry curve recorded at the scan rate 0.05 mV/s (shown in main paper Fig.5). The calculated diffusion coefficients (presented in Table S16) using the slope presented here indicate improved mass transport in the potential range of Co³⁺/Co⁴⁺ redox.



S16. Diffusion coefficients calculated from CV (0.05mV/s) and EIS (cycling at C/25 rate) at different peak potential during oxidation (desodiation) and reduction (sodiation) for the initial cycle. The calculated D_{Na^+} values indicate higher mass transport in the voltage domain corresponding to cobalt redox (Co^{3+}/Co^{4+}).

Samples at different peak potential	Peak current (i _{p)} from CV (A)	D _{Na} * (cm ² /s)	Slope (σ) from EIS	${f D_{Na^+}}\ (cm^2/s)$				
$Na_{0.67}Mn_{0.25}Co_{0.75}O_2$								
3.402 V	0.000027	1.74 X 10 ⁻¹⁰	31.1679	3.16 X 10 ⁻¹¹				
3.697 V	0.000032	2.45 X 10 ⁻¹⁰	37.2391	2.21 X 10 ⁻¹¹				
4.039 V	0.000040	3.83 X 10 ⁻¹⁰	75.2735	5.42 X 10 ⁻¹²				
3.977 V	0.000023	1.27 X 10 ⁻¹⁰	90.2381	3.77 X 10 ⁻¹²				
3.627 V	0.000022	1.16 X 10 ⁻¹⁰	62.5849	7.84 X 10 ⁻¹²				
3.339 V	0.000026	1.62 X 10 ⁻¹⁰	63.4567	7.63 X 10 ⁻¹²				
$Na_{0.67}Mn_{0.5}Co_{0.5}O_2$								
4.045 V	0.000033	1.08 X 10 ⁻¹⁰	143.8121	6.16 X 10 ⁻¹³				
3.980 V	0.000011	1.20 X 10 ⁻¹¹	91.4776	1.52 X 10 ⁻¹²				
1.580 V	0.000052	2.68 X 10 ⁻¹⁰	67.4521	2.80 X 10 ⁻¹²				
1.795 V	0.000066	4.3 X 10 ⁻¹⁰	61.6022	3.36 X 10 ⁻¹²				
$Na_{0.67}Mn_{0.75}Co_{0.25}O_2$								
1.995 V	0.000028	5.95 X 10 ⁻¹¹	34.3556	8.25 X 10 ⁻¹²				
1.750 V	0.000030	6.83 X 10 ⁻¹¹	227.8468	1.87 X 10 ⁻¹³				
1.972 V	0.000031	7.29 X 10 ⁻¹¹	44.4705	4.92 X 10 ⁻¹²				
2.273 V	0.000026	5.13 X 10 ⁻¹¹	50.7029	3.79 X 10 ⁻¹²				

References

- 1. D. Su, C. Wang, H-J. Ahn and G. Wang, *Chemistry- An European J.*, 2013, **19**, 10884-10889.
- 2. R. Dedryve're, D. Foix, S. Franger, S. Patoux, L. Daniel and D. Gonbeau, *J. Phys. Chem. C*, 2010, **114**, 10999-11008.
- M. C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A. R. Gerson and R. Smart, *Appl. Surf. Sci.* 2011, 257, 2717-2730.
- 4. A.I. Nazza, V.Y. Lee, E.M. Engler, R.D. Jacowitz, Y. Tokura, J.B. Torrance, *Phys. C* 1988, **153-155**, 1367-1368.
- 5. X. Wang, M. Tamaru, M. Okubo and A. Yamada, J Phys. Chem. C., 2013, 117, 15545-15551.
- 6. D. Baster, W. Zajac, L. Kondracki, F. Hartman and J. Molenda, *Solid State Ionics*, 2016, **288**, 213-218.
- 7. N. Bucher, S. Hartung, I. Gocheva, Y.L. Cheah, M. Srinivasan and H.E. Hoster, J. Solid State Electrochem., 2013, 17, 1923-1929.
- 8. N. Bucher, S. Hartung, J.B. Franklin, A.M. Wise, L.Y. Lim, H-Y. Chen, J.N. Weker, M. F. Toney and M. Srinivasan, *Chem Mat*, 2016, **28**, 2041-2051.
- 9. D. Carlier, J.H. Cheng, R. Berthelot, M. Guignard, M. Yoncheva, R. Stoynova, B.J. Hwang and C. Delmas, *Dalton Trans.*, 2011, **40**, 9306-9312
- 10. F. R. Beck, Y.Q. Cheng, Z.Bi, M. Feygenson, C.A. Bridges, Z. M. Rosenberg, A. Manthiram, J.B. Good enough, M. P. Paranthaman and A. Manivannan, *J. Electrochem. Soc.*, 2014, **161**, A961-A967.
- 11. X. Xu, S. Ji, R. Gao and J. Liu, RSC Adv., 2015, 5, 51454-51460
- 12. Y-E Zhu, X. Qi, X. Chen, X. Zhou, X. Zhang, J. Wei, Y. Hu and Z. Zhou, *J. Mater. Chem. A.*, 2016, **4**, 11103-11109.