Elucidating the phase transformations and grain growth behavior of O3-type sodium-ion layered oxide cathode materials during high temperature synthesis

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Figure S1: X-ray diffraction patterns of the precursor and precursor+Na₂CO₃ mixtures calcined at different calcination temperatures (the XRD patterns are identical to those presented in Figure 1) Four peaks in this pattern were indexed using the peak positions of the Fe_{0.67}Mn_{0.33}OOH structure, to represent the structural similarity of the reaction intermediates to an oxyhydroxide structure. In the calcination temperature range of 250 - 550 °C, the material transforms to a phase composed of an oxyhydroxide structure through precursor dehydration. Beyond this temperature range, the material starts transforming into a layered oxide structure.



Figure S2: Fe K-edge Fourier transformed EXAFS of the precursor and Na₂CO₃ mixture calcined at 250 °C. The local bonding environment of the reaction intermediate formed at 250 °C resembles the local bonding environment of FeOOH.



Figure S3: X-ray diffraction patterns of the uncalcined precursor and precursor+Na₂CO₃ mixture, and the mixture calcined at different calcination temperatures (the XRD patterns are identical to those presented in Figure 1). Peaks possibly originating from Na₂CO₃ are highlighted with dotted lines in the pattern. When the precursor+Na₂CO₃ mixture is calcined at 250 °C, the most intense peaks belonging to Na₂CO₃ ($2\theta = 30^{\circ}$, 37.9 ° and 41.4 °) diminish in intensity, as well as their intensity ratio changes in the intermediate compared to pristine Na₂CO₃. This indicates that the intermediate could be a sodiated oxyhydroxide composite. Some minor peaks belonging to Na₂CO₃ remain throughout the entire calcination temperature range of 250 °C- 750 °C.



Figure S4: X-ray diffraction patterns of the precursor, Na_2CO_3 and precursor+ Na_2CO_3 mixtures calcined at different calcination temperatures (the XRD patterns are identical to those presented in Figure 1 in the original manuscript). It can be seen that the peak at 16.5 ° originates from Na_2CO_3 (highlighted with the dotted line).



Figure S5: Elemental mapping of $NaNi_{0.33}Fe_{0.33}Mn_{0.33}O_2$ with energy dispersive X-ray spectroscopy (EDS) shows uniform distribution of the constituent elements in the particle.



Figure S6: Ni L-edge spectra in the TEY and FY mode representing the surface and subsurface oxidation state of the samples calcined at different temperatures. The solid lines represent the spectra collected in the TEY mode (surface) and the dotted lines represent the spectra collected in the FY mode (subsurface).



Figure S7: Fe L-edge spectra in the TEY and FY mode representing the surface and subsurface oxidation state of the samples calcined at different temperatures. The solid lines represent the spectra collected in the TEY mode (surface) and the dotted lines represent the spectra collected in the FY mode (subsurface).



Figure S8: Ni K-edge spectra representing the bulk oxidation state of Ni at different calcination temperatures. From precursor to final calcined material, Ni does not show any significant changes in its bulk oxidation state.



Figure S9: Fe K-edge spectra representing the bulk oxidation state of Fe at different calcination temperatures. From precursor to final calcined material, Fe does not show any significant changes in its bulk oxidation state, similar to Ni.



Figure S10: Mn L-edge spectra in the FY mode representing the subsurface oxidation state of the samples calcined at different temperatures. At the sub-surface, Mn shows a gradual oxidation state increase with increasing calcination temperature as observed with the spectral shape and position.



Figure S11: Soft XAS O K-edge spectra of different standard samples of transition metal oxides, Na₂CO₃ and the sample calcined at 850 °C for 6 hours. Each peak observed in the O K-edge spectra can have contributions from multiple TM-O interactions and cannot be deconvoluted in the current analysis. For the reference spectra, NiO powder is from Alfa Aesar (CAS: 1313-99-1, product ID: AA1235930), Fe₂O₃ powder is from Sigma-Aldrich (CAS no.: 1309-37-1, product ID:310050), Mn₃O₄ powder is from Sigma-Aldrich (CAS no.: 1317-35-7, product ID:377473), MnO₂ powder is from Alfa Aesar (CAS no.: 1317-34-6, product ID: 042250.A1), Mn₂O₃ powder is from Alfa Aesar (CAS no.: 1317-34-6, product ID: 087791.A3), MnO powder is from Sigma-Aldrich (CAS no.: 1344-43-0, product ID: 377201), Na₂CO₃ powder is from Acros Organics (CAS no.: 497-19-8, product ID: L13098.36).



Figure S12: Thermogravimetric analysis (TGA) curve of the precursor and precursor + Na_2CO_3 mixture heated from room temperature to 900 °C at a temperature ramping rate of 5 °C/min in air flow.

Weight loss in region I: Surface and interlayer water loss from the precursors

Weight loss in region II: Water loss due to precursor decomposition

Weight loss in region III: Decomposition of Na₂CO₃, water release during sodiation, sodium loss at high temperatures



Figure S13: Apparent diffusion co-efficient measurement of the material during charging at different calcination durations. All the electrochemical tests are done in a NaNFM333| Na half-cell configuration, with 1.0 M NaClO₄ in PC with 5% FEC electrolyte, at a voltage range of 2.0 - 4.3V. Average active material mass loading is 6 mg/cm² and the testing temperature was 22 °C.



Figure S14: (a) Mn L-edge spectra in the TEY mode of the samples calcined at 850 °C for different durations (b) Mn K-edge XANES spectra of the samples calcined at 850 °C for different durations. When the sample is calcined at 850 °C for 24 hours, both surface and bulk level oxidation state decreases, indicating Na/O loss from the material due to prolonged calcination. In the soft XAS spectra, Mn reduction in the 24h sample is evident from the spectral shape change, while in the hard XAS spectra, a 1 eV edge shift to lower energy confirms the bulk oxidation state reduction of Mn.



Figure S15: Bright field scanning transmission electron microscopy (BF-STEM) of the particles calcined at 850 °C for 24 hours. EDS mapping was done on the 17 spots marked in the images which show an inhomogeneous distribution of the transition metal to sodium molar ratio throughout the particles. The results are shown in supplementary Table S6

Table S1: ICPMS results of the $Ni_{0.33}Fe_{0.33}Mn_{0.33}(OH)_{2+x}$ precursor

Ni (mol%)	Fe (mol%)	Mn (mol%)
0.329	0.335	0.336

Sample	Mn ³⁺ wt%	Mn ⁴⁺ wt%	Reduced chi ²	R factor
Precursor	0.642682	0.357318	0.003787	0.044671
250 °C	0.705801	0.294199	0.015315	0.123063
350 °C	0.518657	0.481343	0.005646	0.053424
450 °C	0.263372	0.736628	0.001218	0.014654
550 °C	0.084186	0.915814	0.002258	0.030089
650 °C	0.084085	0.915915	0.002314	0.031457
750 °C	0.045283	0.954717	0.002092	0.027687
850 °C 6h	0.105689	0.894311	0.003962	0.057719
850 °C 12h	0.08482	0.91518	0.002376	0.031865
850 °C 18h	0.046984	0.953016	0.001876	0.022888
850 °C 24h	0.122245	0.877755	0.004894	0.072763

Table S2: Fitting parameters for the Mn L-edge Soft-XAS spectra at different calcination temperatures

Table S3 : Fitting paramters for the linear combination fitting of the Mn Hard X-ray absorption data at different calcination conditions

Sample	Average oxidation state	Reduced chi ²	R factor
Precursor	2.46	0.0003397	0.002135
250 °C	2.87	0.0004311	0.001928
350 °C	2.93	0.0002661	0.0006833
450 °C	3.46	0.0009829	0.0002566
550 °C	3.48	0.0004443	0.0032445
650 °C	3.59	0.0018822	0.0129293
750 °C	3.78	0.0002691	0.0010701
850 °C 6h	3.94	0.0006256	0.0032249
850 °C 12h	4.00	0.0001226	0.0063923
850 °C 24h	3.91	0.0003397	0.005834

Table S4: Lattice parameters obtained from the Rietvelt refinement of the XRD patterns of the samples calcined at different calcination durations:

Sample	a (Å)	b (Å)	c (Å)
850 °C 6h	2.9821	2.9821	16.1398
850 °C 12h	2.9715	2.9715	16.0768
850 °C 18h	2.9718	2.9718	16.1264
850 °C 24h	2.9739	2.9739	16.1297

Calcination Duration	03	Na ₂ CO ₃	Mn ₃ O ₄	NiO
6h	83.69	10.62	4.36	1.33
12h	82.69	9.74	5.23	2.34
18h	85.59	7.22	4.66	2.53
24h	89.34	5.16	3.27	2.23

Table S5: Phase freations (in %) of different phases in the samples calcined at different durations obtained from Rietveld refienment:

			Atomic positions			Atomic	
Calcination Duration		Wyckof f					Displacement Parameter
	Element	position	X	У	Z	Occupancy	b _{eq}
	Na	3a	0	0	0	0.81	0.87
	Ni	3b	0	0	0.50	0.33	0.58
6h	Fe	3b	0	0	0.50	0.33	0.58
	Mn	3b	0	0	0.50	0.33	0.58
	0	6c	0	0	0.23	1.00	1.08
	Na	3a	0	0	0.50	0.83	0.89
	Ni	3b	0	0	0.50	0.33	0.61
12h	Fe	3b	0	0	0.50	0.33	0.61
	Mn	3b	0	0	0.50	0.33	0.61
	0	6c	0	0	0.23	1.00	1.00
	Na	3a	0	0	0	0.82	1.20
	Ni	3b	0	0	0.50	0.33	0.61
18h	Fe	3b	0	0	0.50	0.33	0.61
	Mn	3b	0	0	0.50	0.33	0.61
	0	6c	0	0	0.23	1.00	1.27
	Na	3a	0	0	0	0.85	1.10
	Ni	3b	0	0	0.50	0.33	0.53
24h	Fe	3b	0	0	0.50	0.33	0.53
	Mn	3b	0	0	0.50	0.33	0.53
	0	6c	0	0	0.23	1.00	1.12
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Table S6: Structural Rietveld Refinement results obtained for the samples calcined for different durations. The space group is R-3m.

Sample	BET Surface Area (m ² /g)
850 °C 6h	2.0
850 °C 12h	1.7
850 °C 18h	1.4
850 °C 24h	1.9

Table S7: BET surface area results of the samples calcined at 850 °C for different durations

Spot	Na (mol)	Ni (mol)	Fe (mol)	Mn (mol)	Na : (Ni+ Fe+
Number					Mn)
1	18.21	8.38	10.54	8.89	0.63
2	14.95	8.43	10.14	10.39	0.79
3	18.08	7.93	9.50	7.52	0.56
4	21.15	7.14	8.07	8.48	0.46
5	16.76	11.41	11.73	8.97	0.78
6	15.55	12.05	12.84	11.00	0.94
7	13.20	12.38	16.37	12.91	1.29
8	12.82	12.02	14.48	12.45	1.24
9	9.24	14.41	16.92	15.16	2.05
12	12.54	13.68	17.84	12.55	1.43
13	10.37	15.18	12.38	11.84	1.54
15	22.06	6.52	7.64	6.98	0.39
16	21.33	7.04	8.26	6.90	0.42
17	21.96	9.27	8.11	5.81	0.43

Table S8: Results of elemental mapping performed using STEM- EDS on the spots chosen on the particles calcined at 850 °C for 24 hours. Spots 10, 11 and 14 had too low counts to get a

reasonable signal.