Supplementary Information (SI)

Na_2CoSiO_4 as a cathode material for sodium-ion batteries: structure, electrochemistry and diffusion pathways

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S1 – Rietveld fit and comparison data for Na_2CoSiO_4 synthesised via the solid state method.

Table S(a) orthorhombic, Space group P n a 21 a=10.9560(4)Å b=5.2512(2) Å c= 7.0359(3) Å Vol-404.794 $Å^3$

Formula Weight - 787.980, density: 3.232gm/cm3

Fit wRp – 0.0369, Rp 0.0267, Chi2 – 2.515

Name	X	Y	Z	Ui/Ue*100
Co1	0.1527(4)	0.258(1)	0.637(3)	3.65(19)
Si1	0.405(1)	0.267(3)	0.876 (fixed)	3.7(4)
Na1	0.1670(9)	0.233(2)	0.104(3)	2.0(4)
Na2	0.407(2)	0.262(4)	0.366(3)	4.3(5)
O1	0.322(1)	0.242(4)	0.693(3)	12.3(11)
O2	0.100(2)	0.447(3)	0.408(5)	14.8(14)
O3	0.051(2)	0.283(5)	0.884(4)	10.0(8)
O4	0.142(1)	0.880(3)	0.577(3)	3.5(8)

Table S(b) Monoclinic Space group P n a= 7.03545(30) Å b= 10.9552(4) Å c= 5.25094(19) Å β- 89.954(9)

Fit wRp – 0.0349, Rp 0.0250, X^2 – 2.231

Name	X	Y	Z	Ui/Ue*100
Si1	0.247(4)	0.347(3)	0.006(6)	2.3(4)
Co1	0.001(4)	0.092(2)	0	9.8(9)
Na1	0.758(7)	0.327(3)	0.981(12)	1.0(12)
Na2	0.486(7)	0.085(2)	1.005(9)	0.2(11)
O1	0.702(7)	0.295(3)	0.433(15)	4.3(26)
O2	0.285(6)	0.345(4)	0.313(7)	0.9(8)
O3	0.548(6)	0.083(2)	0.462(11)	5.4(18)
O4	0.945(6)	0.109(4)	0.363(2)	0.7(8)
Si2	0.250(4)	0.847(3)	0.003(6)	2.3(4)
Co2	-0.0047(34)	0.593(1)	0.019(4)	2.3(6)
Na3	0.772(6)	0.848(3)	0.969(10)	2.0(16)
Na4	0.498(8)	0.612(2)	0.969(7)	3.0(14)
O5	0.714(6)	0.797(3)	0.441(10)	2.3(20)
O6	0.273(5)	0.860(4)	0.311(6)	0.9(8)

O7	0.581(6)	0.565(3)	0.393(8)	5.4(18)
O8	0.946(6)	0.603(4)	0.387(4)	0.7(8)

S2 –Rietveld refinement and atomic positions of Na_2CoSiO_4 (900°C with NaCl flux agent)

Figure S(a) – Observed and calculated powder XRD pattern of Na_2CoSiO_4 (900°C with NaCl flux agent)

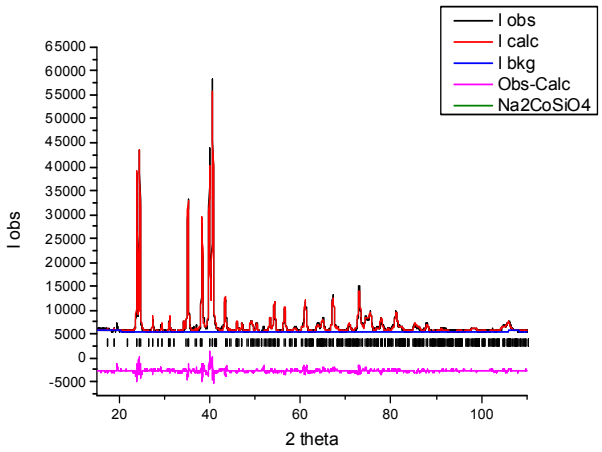


Table S(c) – Atomic positions from Rietveld refinement of Na_2CoSiO_4 (900°C with NaCl flux agent)

Name	X	Y	Z	Ui/Ue*100	Site
Si1	0.2546(31)	0.3348(13)	-0.002(4)	0.7(7)	1
Co1	-0.0034(24)	0.0886(10)	0	2.4(4)	1
Na1	0.760(4)	0.3377(18)	0.984(11)	0.9(10)	1
Na2	0.493(5)	0.0832(23)	0.991(11)	2.6(11)	1
O1	0.7069(36)	0.2858(17)	0.4525(110)	5.0(14)	1
O2	0.2673(40)	0.3493(31)	0.3062(41)	1.4(14)	1
O3	0.5481(27)	0.0834(15)	0.4246(74)	0.8(17)	1
O4	0.9477(41)	0.1098(35)	0.3669(21)	9.2(23)	1
Si2	0.2493(25)	0.8569(13)	0.009(5)	0.5(6)	1
Co2	-0.0054(21)	0.6026(9)	-0.003(5)	3.8(4)	1
Na3	0.749(5)	0.8521(21)	0.966(11)	5.3(12)	1
Na4	0.481(4)	0.5966(22)	1.001(8)	1.7(9)	1
O5	0.7164(38)	0.8079(21)	0.4332(120)	6.9(18)	1
O6	0.2801(41)	0.8431(37)	0.3149(52)	6.1(20)	1
O7	0.5969(32)	0.5612(15)	0.4428(105)	3.1(17)	1
O8	0.9388(36)	0.6025(32)	0.3650(48)	3.1(18)	1

S3 – Reitveld refinement and atomic positions from Rieteld refinement of Na_2CoSiO_4 (900°C, no NaCl flux agent during anneal)

Figure S(b) – Observed and calculated powder XRD pattern of Na_2CoSiO_4 (900°C, no NaCl flux agent during anneal)

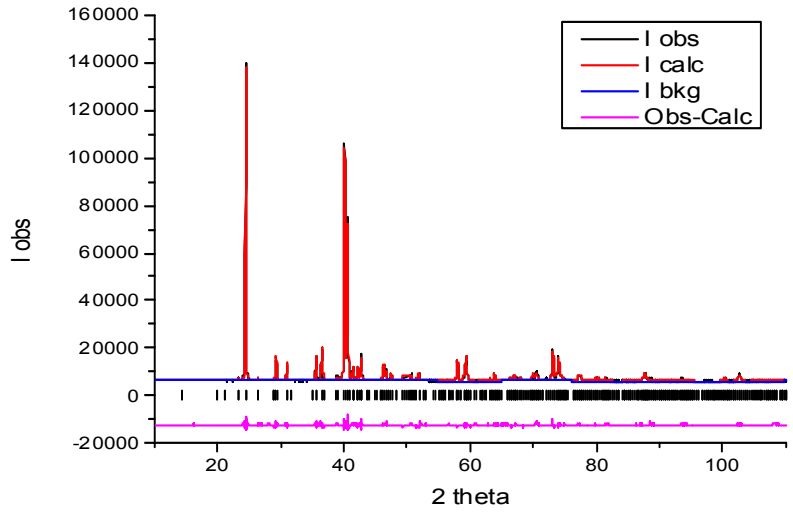


Table S(d) – Atomic positions from Rietveld refinement of Na_2CoSiO_4 (900°C, no NaCl flux agent during anneal)

Name	X	Y	Z	Ui/Ue*100	Fractn
Co1	0.9715(4)	0.8145(5)	0.700955	3.34(17)	0.523(9)
Si1	0.9715(4)	0.8145(5)	0.700955	3.34(17)	0.477(9)
Co2	0.2655(4)	0.0596(5)	0.2781(7)	3.00(18)	0.477(9)
Si2	0.2655(4)	0.0596(5)	0.2781(7)	3.00(18)	0.523(9)
Na1	0.4881(15)	0.0681(18)	0.6816(56)	0.27(25)	0.503(45)
Na2	0.5045(16)	0.0408(20)	0.7742(54)	0.27(25)	0.466(45)
Na3	0.7465(9)	0.3128(12)	0.1809(23)	0.27(25)	0.620(11)
Na4	0.7951(19)	0.3073(18)	0.3746(44)	0.27(25)	0.286(9)
O1	0.0656(8)	0.9119(7)	0.8030(17)	0.28(34)	1
O2	0.0192(11)	0.7801(7)	0.4238(29)	8.10(56)	1
O3	0.2396(8)	0.9595(8)	0.1276(18)	1.39(39)	1
O4	0.7913(8)	0.8387(8)	0.8456(20)	1.81(39)	1

S4 Summary of the Rietveld refinement data for Na_2CoSiO_4 made by the solid state and coprecipitation methods.

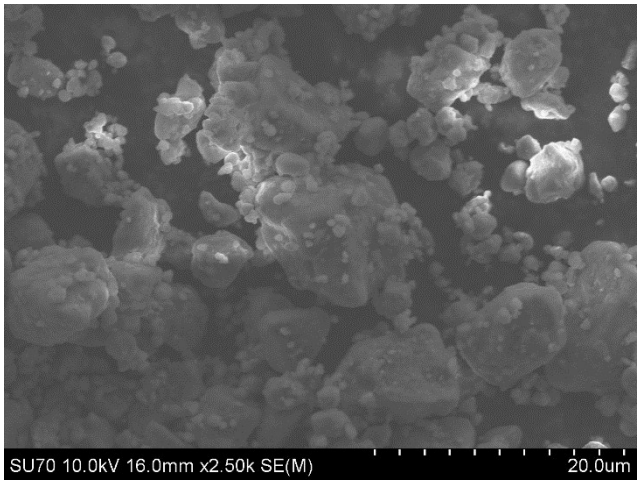
Table S(e) – Summary of crystallographic data derived from Rietveld refinement

	Solid State	Coprecipitation + NaCl	Coprecipitation
Firing Temperature (°C)	800	900	900
Space group	Pn	Pn	Pbca

	Monoclinic	Monoclinic	Orthorhombic
Lattice Parameters			
a (Å)	7.0355(3)	7.0433(2)	10.4543(3)
b(Å)	10.9552(4	10.9128(4)	14.4724(3)
c(Å)	5.2509(2)	5.2396(2)	5.2274(2)
β	89.954(9)	90.02(1)	90.00(0)
Vol	404.717(28)	402.73(3)	790.90(4)
Average Bond lengths			
Si-O (Å)	1.63175	1.62025	1.763
Co-O (Å)	1.9545	1.9555	1.834
Na-O (Å)	2.41	2.4475	2.514
Na-O (Å)	2.3475	2.2975	2.362
Si-O (Å)	1.63175	1.621	1.763
Co-O (Å)	1.95725	1.92975	1.834

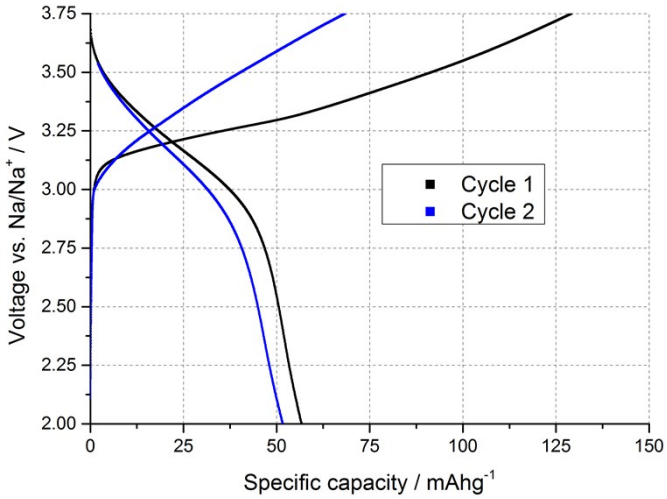
S5

Figure S(b) – SEM image of Na_2CoSiO_4 synthesised via the solid-state method, annealing at 800°C under flowing N_2



S6

Figure S(c) - Voltage vs. specific capacity plot for Na_2CoSiO_4 made by a coprecipitation method (NaCl removed, dried at 120°C)



S7

Figure S(d) - Voltage vs. specific capacity plot for the first two cycles of Na_2CoSiO_4 material (500°C anneal with NaCl flux agent). Inset (right) is a specific discharge capacity vs. cycle number plot.

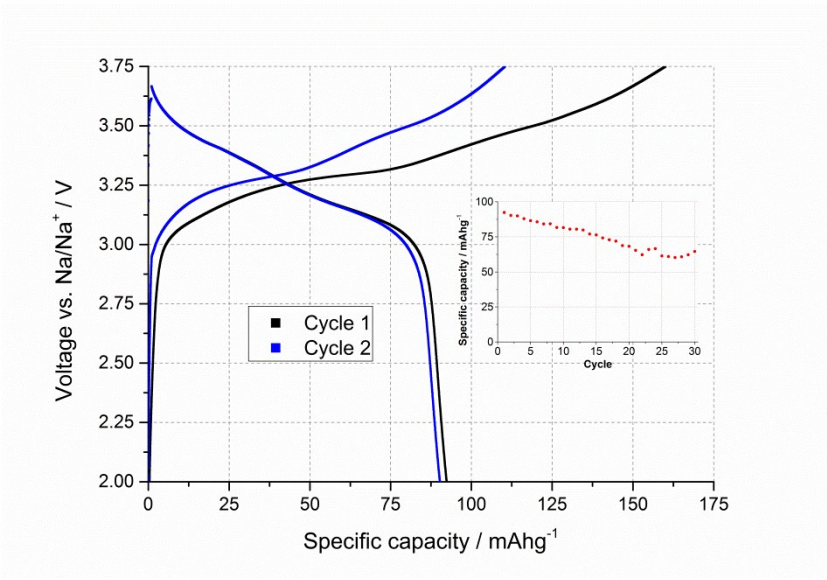


Figure S(e) - Voltage vs. specific capacity plot for the first two cycles of Na_2CoSiO_4 material (NaCl removed before 500°C anneal). Inset (right) is a specific discharge capacity vs. cycle number plot.

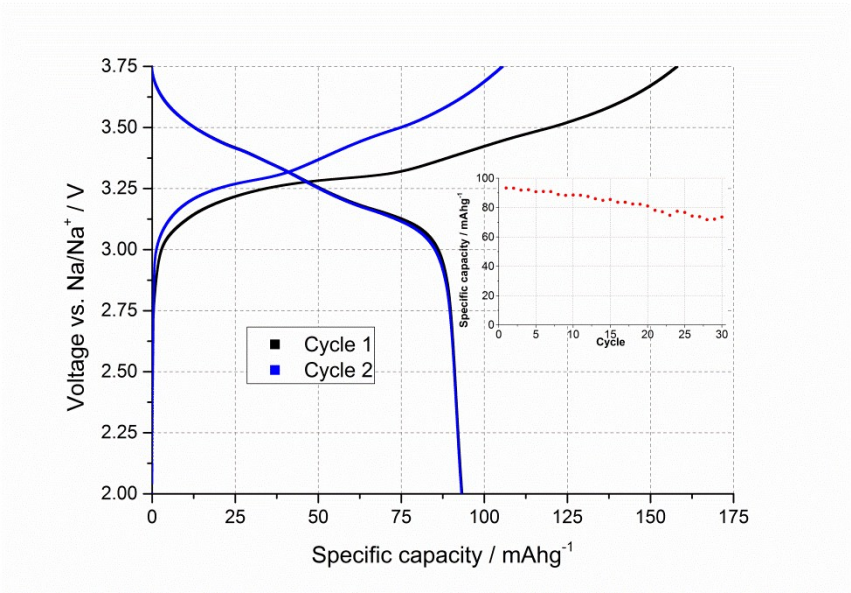


Figure S(f) – Differential capacity vs. voltage plot (left, first cycle only), voltage vs. specific capacity plot (centre) and specific discharge capacity vs. cycle number (right) for first two cycles of Na_2CoSiO_4 material synthesised at 900°C in the presence of the NaCl flux agent.

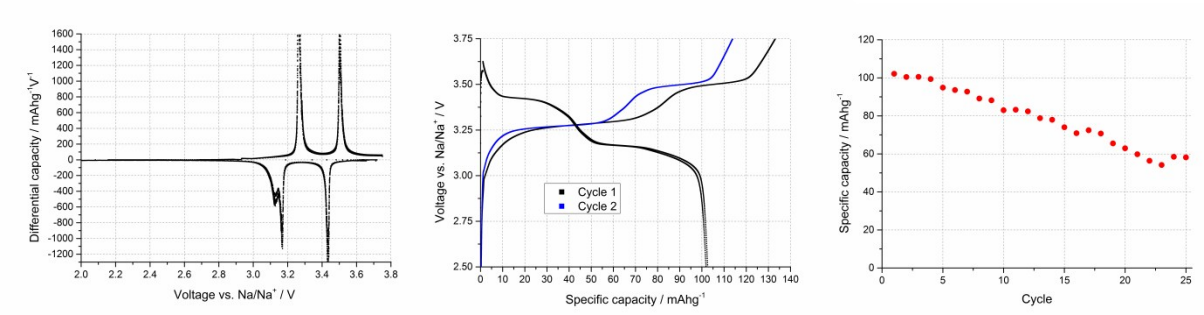


Figure S(g) – Differential capacity vs. voltage plot (left, first cycle only), voltage vs. specific capacity plot (centre) and specific discharge capacity vs. cycle number (right) for first two cycles of Na_2CoSiO_4 material synthesised at 900°C with NaCl removed before the anneal.

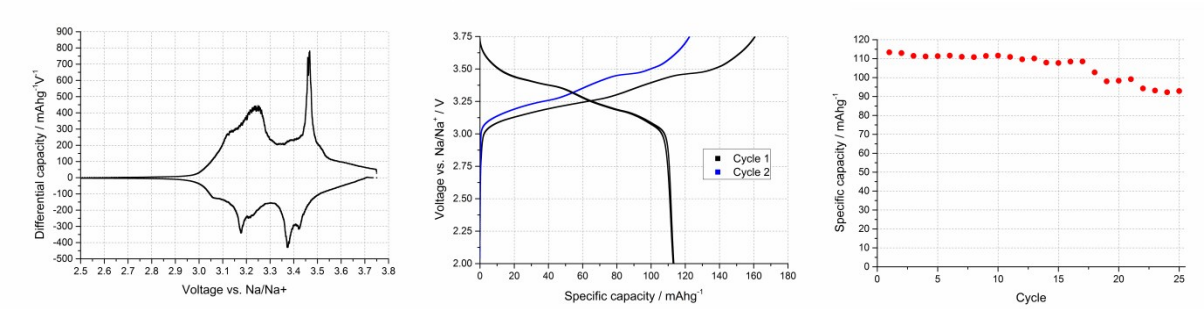


Table S(f): Potential set derived for defect calculations. A, ρ and C are Buckingham potential paramters, Y is the core charge split and k the spring constant strength.

Interaction	*A* (eV)	*ρ* (Å)	*C* (eV.Å^6)	*Y* (e)	*K* (eV.Å^{-2})
Na-O	1497.830598	0.287483	0	1	99999
Co-O	696.3	0.3362	0	0	10.74
Si-O	1345.432113	0.32052	10.66	4	99999
O-O	22764.3	0.149	43	0.96	65

Representative defect equations in Kroger-Vonk notation

Frenkel

$Na_{Na}^{\times} \rightarrow V_{Na}^{'} + Na_i^{\bullet}$

$O_O^{\times} \rightarrow V_O^{\bullet\bullet} + O_i^{''}$

Full Schottky

$2Na_{Na}^{\times} + Co_{Co}^{\times} + Si_{Si}^{\times} + 4O_O^{\times} \rightarrow 2V_{Na}^{'} + V_{Co}^{''} + V_{Si}^{''''} + 4V_O^{\bullet\bullet} + Na_2FeSiO_4$

Na/Co anti-site

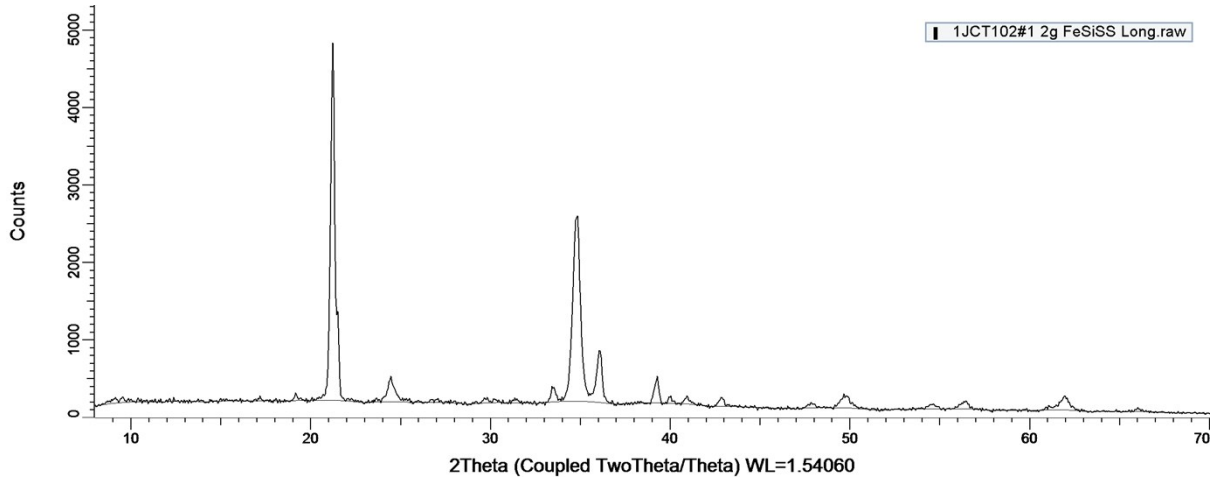
$Na_{Na}^{\times} + Co_{Co}^{\times} \rightarrow Co_{Na}^{\bullet} + Na_{Co}^{'}$

S10

Table S(g): Activation barrier for Na^+ ion diffusion in $Na_{1.8}CoSiO_4$, separated into migration parallel to the *a*, *b* and *c* unit cell parameters.

Direction	E_a(eV)
a	0.22
b	0.21
c	0.21

S11



FigS11a Na_2FeSiO_4 XRD pattern showing a different crystal structure to the Na2CoSiO4 which can be fitted with a cubic superstructure unit cell.

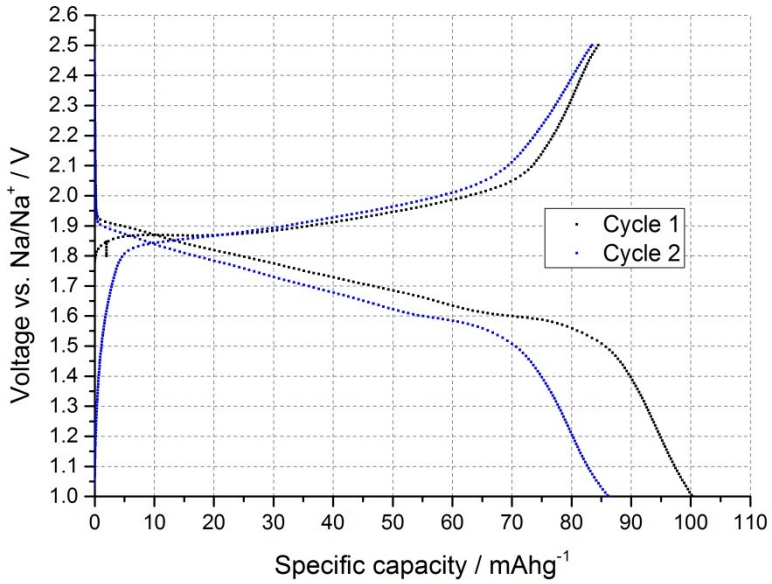
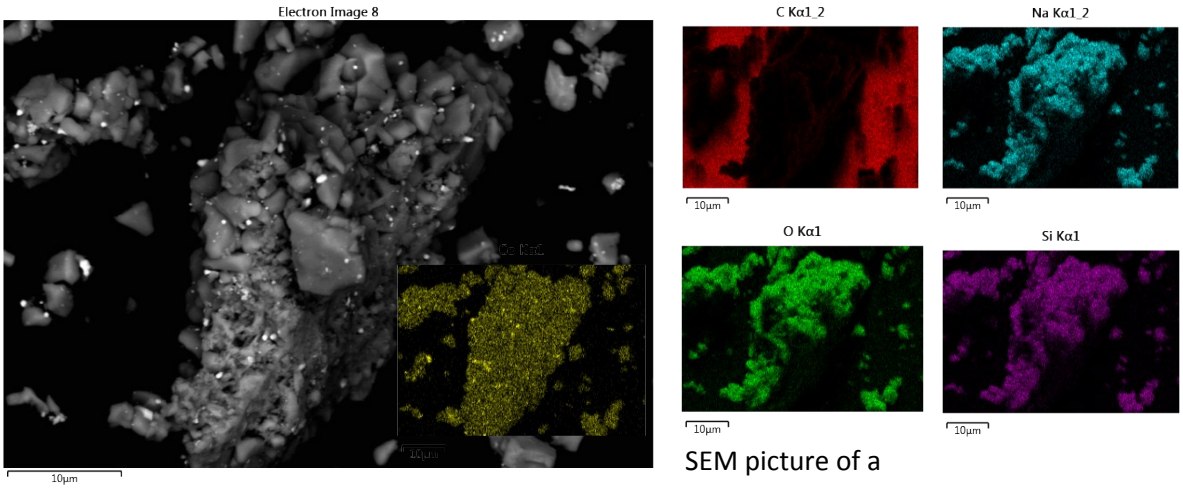


Fig S11b Na_2FeSiO_4 electrochemistry in a sodium metal anode cell with 0.5MNaClO4 in PC electrolyte

S12a



SEM picture of a Na_2CoSiO_4 synthesised at 800°C with excess carbon showing the distribution of cobalt metal through the sample, which is obtained by carbothermal reduction.

S12b

Table 1: Summary data from CHN analysis of samples synthesised via the coprecipitation method

NaCl removed before / after anneal	Annealing temperature / °C	C / %wt.	H / %wt.	N / %wt.
Before	500	0.75	0.1	0.17
After	500	0.76	0.11	0.13
Before	700	0.28	0	0
After	700	0.45	0	0
Before	900	0.11	0	0
After	900	0.23	0	0