Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

P-type $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$ Materials: Linking Synthesis to Structure and Electrochemical Performance

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1. Energy Dispersive X-ray Spectroscopy

For the verification of the stoichiometry, Energy Dispersive X-ray analyses (EDX) were performed on the $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$ (NaNCM) powder.

Table SI-1. Results for the chemical characterization via energy dispersive X-ray analyses (EDX) performed on the $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$.

Stoichiometry	O	Na	Mn	Co	Ni
Measured	32.85	10.75	37.18	6.59	12.62
Calculated	2.053125	0.467391	0.6772313	0.111885	0.214991
Normalized	2.00	0.46	0.66	0.11	0.21

2. Rietveld Refinement

2.1 700 °C

R-Values

Rexp	1.93	Rwp	4.59	Rp	3.42	GOF	2.38
Rexp`	3.31	Rwp`	7.87	Rp`	6.32	DW	0.36

Quantitative Analysis - Rietveld

Phase 1: P3	100.000 %

Background

One on X		49400(5000)
Chebychev polynomial, Coefficient	0	1070(140)
	1	640(110)
	2	-467(48)
	3	304(19)
	4	-50.0(80)

Corrections

Specimen displacement	0.2580(40)
LP Factor	0

Structure 1

Phase name	P3
R-Bragg	1.505
Spacegroup	R3m
Scale	0.005752(87)
Cell Mass	293.993
Cell Volume (Å^3)	119.862(18)
Wt% - Rietveld	100.000

Lattice parameters

a (Å)	2.86618(12)
c (Å)	16.8478(20)

Site	Np	x	y	z	Atom	Occ	Beq
Na1	3	0.00000	0.00000	0.17216	Na+1	0.45	0
Ni1	3	0.00000	0.00000	0.00000	Ni+2	0.22	0
Co1	3	0.00000	0.00000	0.00000	Co+3	0.11	0
Mn1	3	0.00000	0.00000	0.00000	Mn+4	0.66	0
O1	3	0.00000	0.00000	-0.39121	O-2	1	0
O2	3	0.00000	0.00000	0.39121	O-2	1	0

2.2 750 °C

R-Values

Rexp	3.97	Rwp	5.83	Rp	4.59	GOF	1.47
Rexp`	1.84	Rwp`	2.70	Rp`	2.39	DW	0.92

Quantitative Analysis - Rietveld

Phase 1: P3	69.54(42) %

Phase 2: P2 30.46(42) %

Background

One on X		47000(1200)
Chebychev polynomial, Coefficient	0	-742(33)
	1	1094(28)
	2	-477(12)
	3	180.0(49)
	4	-63.0(22)

Corrections

Specimen displacement	-0.0091(38)
LP Factor	0

Structure 1

Phase name	P3
R-Bragg	2.495
Spacegroup	R3m
Scale	0.001093(13)
Cell Mass	293.993
Cell Volume (Å^3)	119.062(28)
Wt% - Rietveld	69.54(42)

Lattice parameters

a (Å)	2.86040(21)
c (Å)	16.8030(31)

Site	Np	x	y	z	Atom	Occ	Beq
Na1	3	0.00000	0.00000	0.17121	Na+1	0.45	0
Ni1	3	0.00000	0.00000	0.00000	Ni+2	0.22	0
Co1	3	0.00000	0.00000	0.00000	Co+3	0.11	0
Mn1	3	0.00000	0.00000	0.00000	Mn+4	0.66	0
O1	3	0.00000	0.00000	0.39121	O-2	1	0
O2	3	0.00000	0.00000	-0.39121	O-2	1	0

Structure 2

Phase name	P2
R-Bragg	3.413
Spacegroup	P63/mmc
Scale	0.001079(17)
Cell Mass	195.995
Cell Volume (Å^3)	79.210(14)
Wt% - Rietveld	30.46(42)

Lattice parameters

a (Å)	2.85936(18)
c (Å)	11.1869(13)

Site	Np	x	y	z	Atom	Occ	Beq
Mn1	2	0.00000	0.00000	0.00000	Mn+4	0.66	0
Ni1	2	0.00000	0.00000	0.00000	Ni+2	0.22	0
Co1	2	0.00000	0.00000	0.00000	Co+3	0.11	0
Na1	2	0.00000	0.00000	0.25000	Na+1	0.225	0
Na2	2	0.33333	0.66667	0.75000	Na+1	0.225	0
O1	4	0.33333	0.66667	0.08720	O-2	1	0

2.3 800 °C

R-Values

Rexp	2.03	Rwp	6.06	Rp	4.32	GOF	2.98
Rexp`	2.09	Rwp`	6.21	Rp`	4.76	DW	0.34

Quantitative Analysis - Rietveld

Phase 1: P3	100.000 %

Background

One on X	77300(2100)
Chebychev polynomial, Coefficient	0 33(57)
	1 1474(50)
	2 -577(20)
	3 222.2(88)

Corrections

Specimen displacement	0.12778(74)
LP Factor	0

Structure 1

Phase name	P2
R-Bragg	3.195
Spacegroup	P63/mmc
Scale	0.017579(94)
Cell Mass	195.995
Cell Volume (Å^3)	79.61964
Wt% - Rietveld	100.000

Lattice parameters

a (Å)	2.86289(03)
c (Å)	11.21708(93)

Site	Np	x	y	z	Atom	Occ	Beq
Mn1	2	0.00000	0.00000	0.00000	Mn+4	0.66	0
Ni1	2	0.00000	0.00000	0.00000	Ni+2	0.22	0
Co1	2	0.00000	0.00000	0.00000	Co+3	0.11	0
Na1	2	0.00000	0.00000	0.25000	Na+1	0.225	0
Na2	2	0.33333	0.66667	0.75000	Na+1	0.225	0
O1	4	0.33333	0.66667	0.08720	O-2	1	0

2.4 850 °C

R-Values

Rexp	2.94	Rwp	7.39	Rp	5.01	GOF	2.51
Rexp`	5.48	Rwp`	13.77	Rp`	10.34	DW	0.56

Quantitative Analysis - Rietveld

Phase 1: P3	100.000 %

Background

One on X	14974.08

Chebychev polynomial, Coefficient	0	568.9367
	1	192.228
	2	-76.04768
	3	25.80076

Corrections

Specimen displacement	0.1330279
LP Factor	0

Structure 1

Phase name	P2
R-Bragg	5.529
Spacegroup	P63/mmc
Scale	0.00820727(66)
Cell Mass	195.995
Cell Volume (Å^3)	79.61123
Wt% - Rietveld	100.000

Lattice parameters

a (Å)	2.86315(10)
c (Å)	11.2138614

Site	Np	x	y	z	Atom	Occ	Beq
Mn1	2	0.00000	0.00000	0.00000	Mn+4	0.66	0
Ni1	2	0.00000	0.00000	0.00000	Ni+2	0.22	0
Co1	2	0.00000	0.00000	0.00000	Co+3	0.11	0
Na1	2	0.00000	0.00000	0.25000	Na+1	0.225	0
Na2	2	0.33333	0.66667	0.75000	Na+1	0.225	0
O1	4	0.33333	0.66667	0.08720	O-2	1	0

2.5 900 °C

R-Values

Rexp	2.89	Rwp	9.74	Rp	6.21	GOF	3.37
Rexp`	5.17	Rwp`	17.42	Rp`	12.38	DW	0.51

Quantitative Analysis - Rietveld

Phase 1: P3	100.000 %

Background

One on X		14621.81
Chebychev polynomial, Coefficient	0	571.7795
	1	179.0797
	2	-71.77887
	3	26.75187

Corrections

Specimen displacement	0.1176249
LP Factor	0

Structure 1

Phase name	P2
R-Bragg	7.503

Spacegroup	P63/mmc
Scale	0.008791748(67)
Cell Mass	195.995
Cell Volume (Å^3)	79.61510
Wt% - Rietveld	100.000

Lattice parameters

a (Å)	2.86401(23)
c (Å)	11.20766(29)

Site	Np	x	y	z	Atom	Occ	Beq
Mn1	2	0.00000	0.00000	0.00000	Mn+4	0.66	0
Ni1	2	0.00000	0.00000	0.00000	Ni+2	0.22	0
Co1	2	0.00000	0.00000	0.00000	Co+3	0.11	0
Na1	2	0.00000	0.00000	0.25000	Na+1	0.225	0
Na2	2	0.33333	0.66667	0.75000	Na+1	0.225	0
O1	4	0.33333	0.66667	0.08720	O-2	1	0

Table SI-2. Comparison of the 1st charge capacity, Na content equivalent and lattice parameters of $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$ (NaNCM) materials annealed from 700 °C to 900 °C, for 6.

T (°C)	Structure type	Capacity 1st charge (mAh g^{-1})	Na eq. per mole of NaNCM	*a* axis (Å)	*c* axis (Å)
700	P3	113.2263	0.414	2.86618	16.8478
750	P3	142.16	0.5198	2.86040	16.8030
750	P2			2.85936	11.1869
800	P2	137.8604	0.5041	2.86289	11.21708
850	P2	133.4476	0.488	2.863151	11.21386
900	P2	132.0907	0.483	2.864012	11.20766

3. Influence of Annealing Time on the Structure of NaNCM

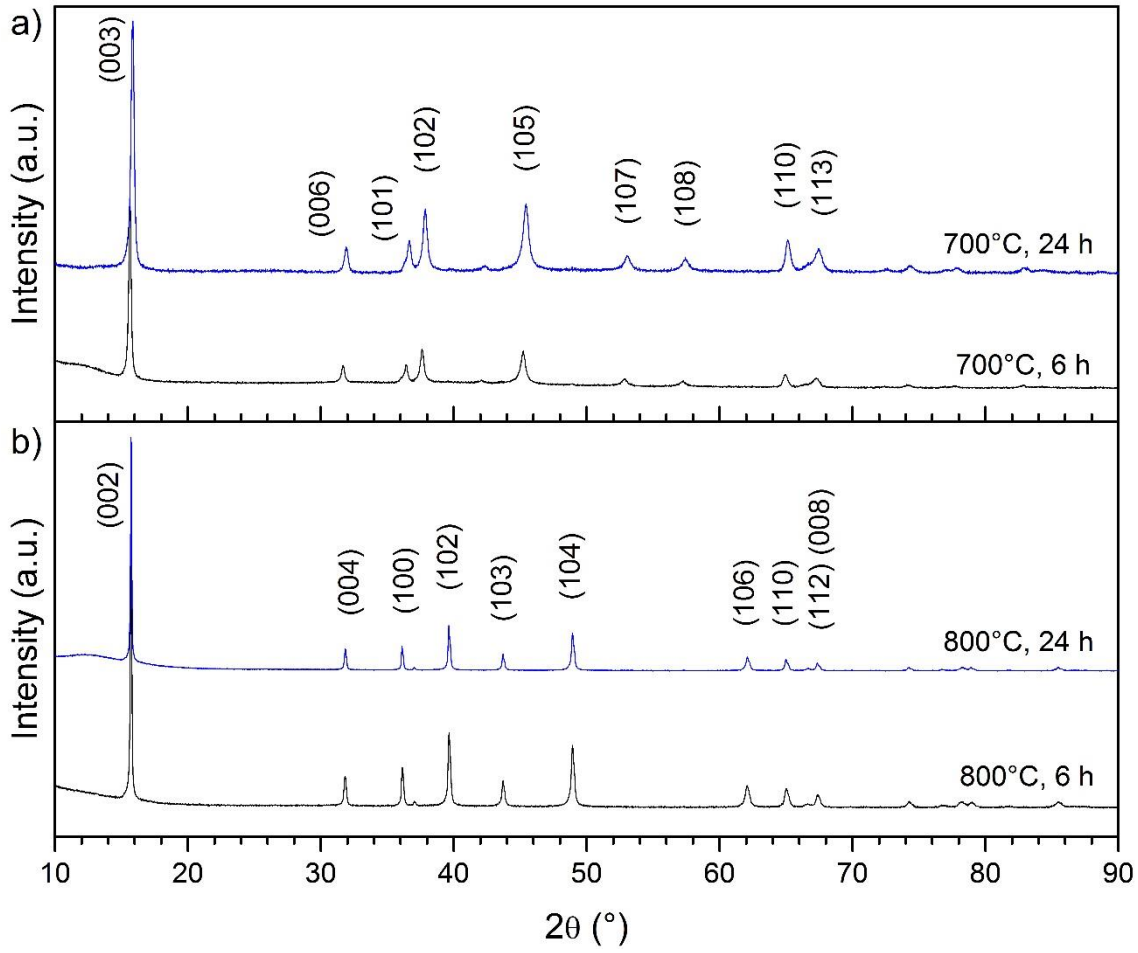

Figure SI-1. X-ray diffraction patterns of $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$ materials annealed at a) 700 °C and b) 800 °C, for 6 or 24 h.

4. Influence of Annealing Time on the Particle Morphology

4.1 P3-type Material

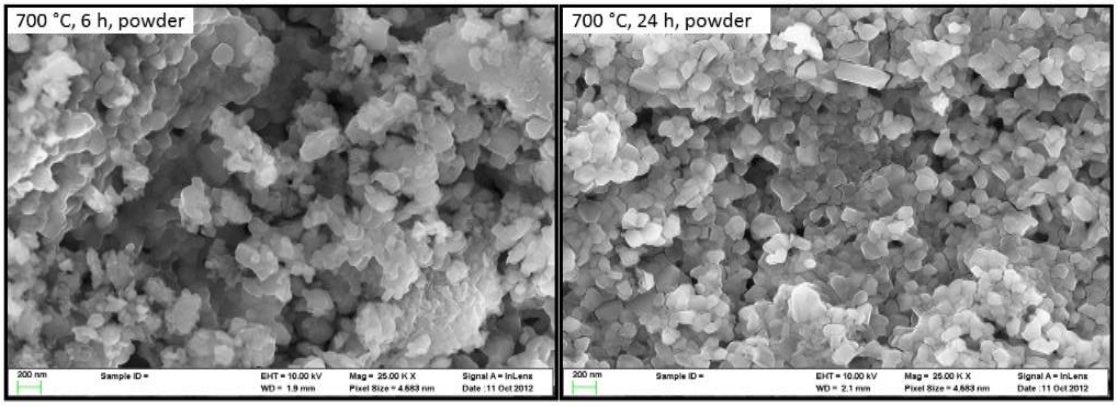

Figure SI-2. Scanning Electron Microscopy images of P3-type $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$ annealed at 700 °C for 6h or 24h.

In general, both P3-type materials synthesized at 700°C, are composed of nano-sized particles with flake-like morphology. The sample annealed at 700 °C for 6 hours has smaller particles and an average particle size is between 50 and 200 nm compared to 100 – 300 nm for the sample annealed for 24 hours.

4.2 P2-type material

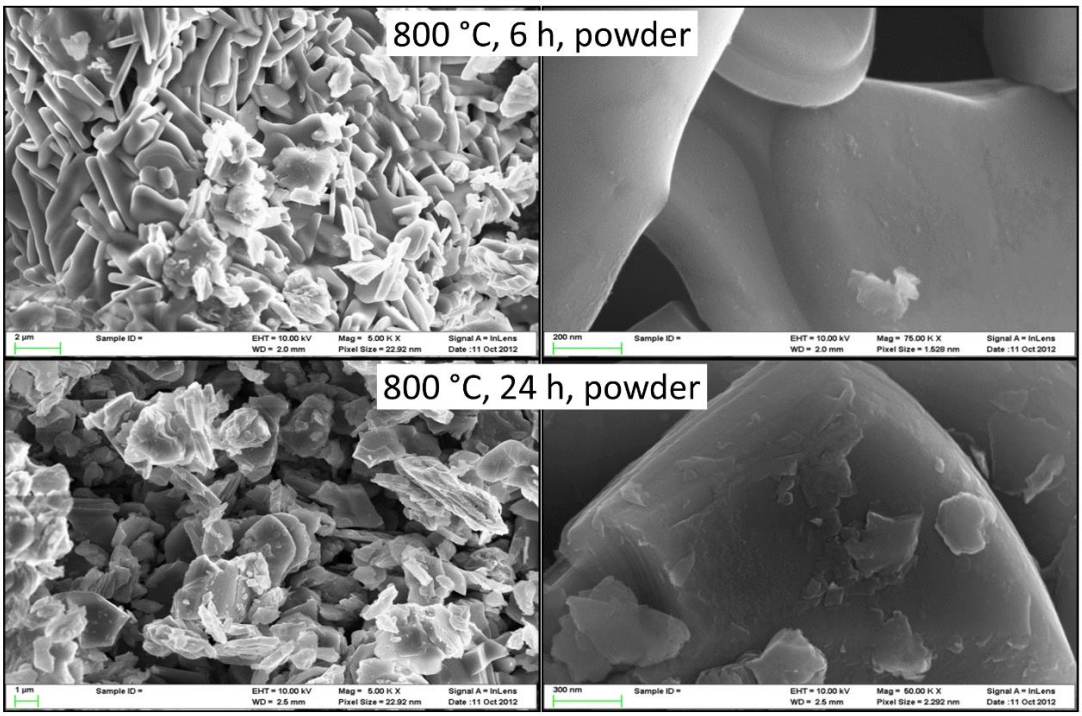

Figure SI-3. Scanning Electron Microscopy images of P2-type $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$ annealed at 800 °C for 6h or 24 h at high and low magnification.

All P2- NaNCM samples annealed at 800 °C for 6 or 24 h are composed of flake-like particles and all samples of particles with an average particle size of 1 – 3 μm.

5. Influence of Annealing Time on the Electrochemical Performance

Figure SI-4 shows the electrochemical performance of the P3-type NaNCM material annealed at 700 °C, for 6 or 24 h. Both materials reveal a very similar electrochemical behavior in terms of capacity, cycling stability and efficiency and exhibit a higher initial capacity fading up to the 20th cycle leading, e.g., to a capacity retention of about 75% for the material annealed at 700°C for 6 h (700_{6h}). Between the 91st and 141st cycle the 700_{6h} material delivers slightly higher discharge capacities of about 95 mAh g^{-1}. The final capacity retention is 55%, accounting for 80 mAh g^{-1} as discharge capacity in the 230th cycle.

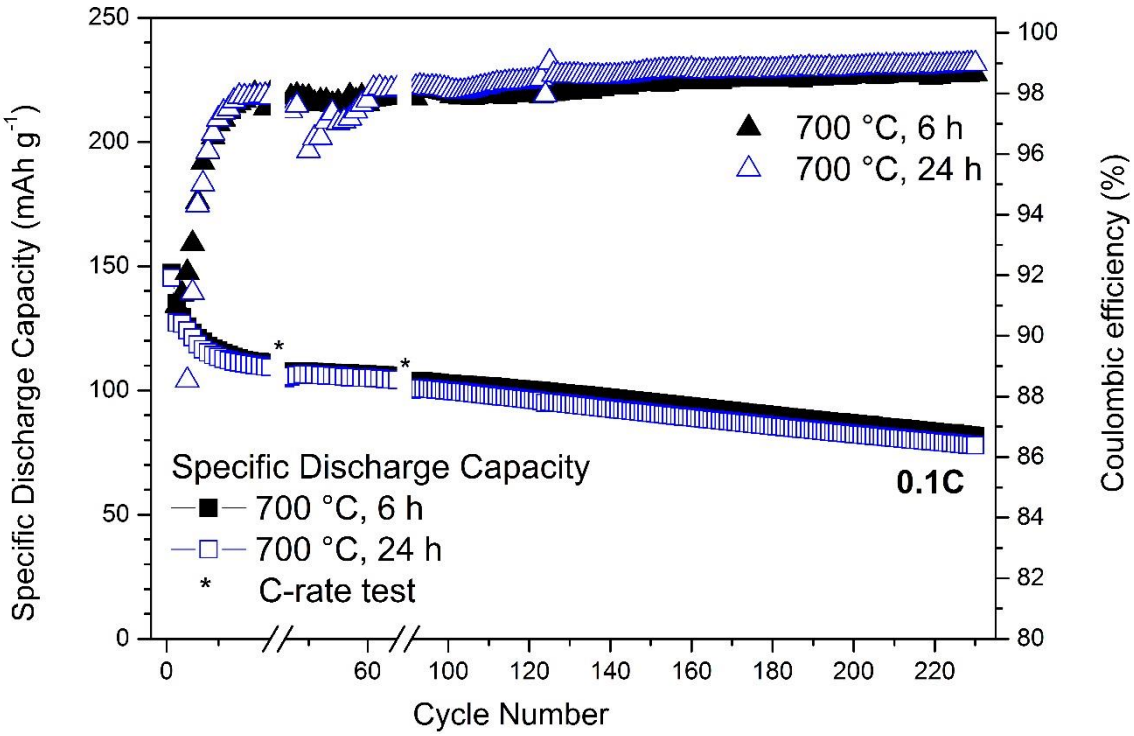

Figure SI-4: Specific discharge capacity of $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$ annealed at 700 °C for 6 and 24 h. Cut-off limits: 4.3 – 2.1 V (*vs*. Na/Na$^+$). Reference and counter electrode: Na. Electrolyte: 1M $NaPF_6$ in PC. Temperature: 20 ± 2°C. Cycles 1-20, 46-65 and 91-230 were performed at 0.1C (12 mA g^{-1}). Cycles 21-45 and 66-90: C-rate test performed at 0.2C (24 mA g^{-1}), 0.5C (61 mA g^{-1}), 1C (123 mA g^{-1}), 2C (246 mA g^{-1}) and 5C (615 mA g^{-1}).

The potential profiles in Figure SI-5 reveal that the annealing time also has only a minor influence on the energy efficiency and rate capability of the P3-type NaNCM materials.

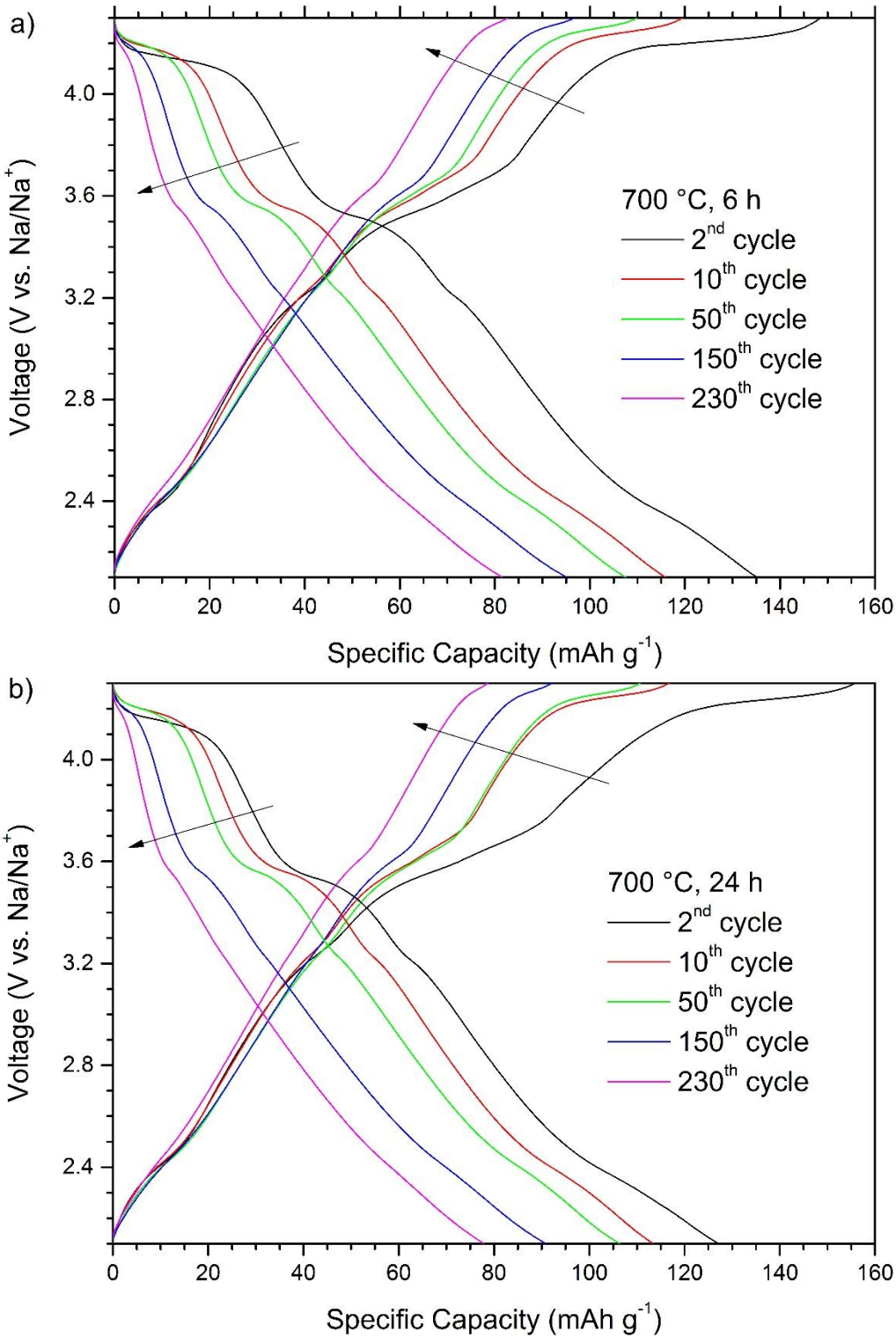

Figure SI-5: Potential profiles of $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$ annealed at 700 °C for a) 6 h or b) 24 h. The potential profile of the 2nd, 10th, 50th, 150th and 230th cycle at 0.1C (12 mA g^{-1}) are shown. Cut-off limits: 4.3−2.1 V (vs Na/Na^+). Reference and counter electrodes: Na. Electrolyte: 1M $NaPF_6$ in PC. Temperature: 20 ± 2 °C. The arrows indicate the voltage curve evolution during cycling.