Influence of Na/Mn arrangements and P2/P'2 phase ratio on electrochemical performance of Na_xMnO_2 – cathode for sodium-ion batteries.

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Rietveld refinement

Constraints for Rietveld Refinements:

• Isotropic displacement values (Uiso) of sodium sites were constrained to be equivalent.

• Refined isotropic displacement values (Uiso) for each element sites were constrained to be equivalent in both phases in biphasic samples: NMO_h/m_3/7 and NMO_h/m_5/5.

• The site occupancy fractions (occ) values for transition metals were fixed at the nominal stoichiometric values for NMO_h/m_3/7 and NMO_h/m_5/5 samples.

• The occ values for oxygen were fixed at the nominal stoichiometric value.

Table S1. X-Ray diffraction and neutron powder diffraction fitting results for NMO samples.

NMO_h/m_3/7

P2'- C2/c phase, unit cell parameters [Å]; *a* = 2.8348(5), *b* =5.2644(8), *c*= 11.2057(1), β = 90.436(2)						
atom	Wyckof index	x	y	z	U_{iso}	occ
Mn	4 a	0.000000	0.000000	0.000000	0.0050(2)	1
$Na_e(2)$	4 e	0.000000	0.3230(8)	0.250000	0.0275(3)	0.499(1)
$Na_f(1)$	4 e	0.000000	-0.07578(2)	0.250000	0.0275(9)	0.202(5)
O	8 f	0.00068(2)	0.6485(6)	0.09059(1)	0.0125(4)	1
P2 - P63/mmc, unit cell parameters [Å]; *a*=2.8787(5), *b* = 2.8787(5), *c*= 11.1655(9)						
atom	Wyckof index	x	y	z	U_{iso}	occ
O	4 f	0.333333	0.666667	0.5922(7)	0.0125(4)	1
$Na_e(2)$	2 c	0.333333	0.666667	0.250000	0.0275(3)	0.255(2)
$Na_f(1)$	2 b	0.000000	0.000000	0.250000	0.0275(3)	0.225(5)
Mn	2 a	0.000000	0.000000	0.000000	0.0050(2)	1

Chi squared, $\chi^2 = 5.91$

NMO_h/m_5/5

P2'- C2/c phase, unit cell parameters [Å]; *a* = 2.8369(4), *b* = 5.2642(1), *c*= 11.1769(1), β = 90.293(1)						
atom	Wyckof index	x	y	z	U_{iso}	occ
Mn	4 a	0.000000	0.000000	0.000000	0.0091(7)	1
$Na_e(2)$	4 e	0.000000	0.3295(3)	0.250000	0.0498(5)	0.488(1)
$Na_f(1)$	4 e	0.000000	-0.06826(6)	0.250000	0.0498(5)	0.276(4)
O	8 f	-0.00036(1)	0.6494(2)	0.08974(1)	0.0135(3)	1
P2 - P63/mmc, unit cell parameters [Å]; *a* = 2.8797(7), *b* = 2.8797(7), *c* = 11.1651(5)						
atom	Wyckof index	x	y	z	U_{iso}	occ
O	4 f	0.333333	0.666667	0.5920(7)	0.0135(3)	1
$Na_e(2)$	2 c	0.333333	0.666667	0.250000	0.0412(4)	0.307(3)
$Na_f(1)$	2 b	0.000000	0.000000	0.250000	0.0412(4)	0.227(4)
Mn	2 a	0.000000	0.000000	0.000000	0.0091(7)	1

Chi squared, $\chi^2 = 4.11$

NMO_h_1

P2 - P63/mmc, unit cell parameters [Å]; *a* = 2.8759(1), *b* = 2.8759(1), *c* = 11.1345(1)						
atom	Wyckof index	x	y	z	U_{iso}	occ
O	4 f	0.333333	0.666667	0.5913(6)	0.0177(12)	1
$Na_e(2)$	2 c	0.333333	0.666667	0.250000	0.0420(4)	0.327(5)
$Na_f(1)$	2 b	0.000000	0.000000	0.250000	0.0420(4)	0.270(3)
Mn	2 a	0.000000	0.000000	0.000000	0.0085(3)	0.927(6)

Chi squared, $\chi^2 = 5.49$

SEM/EDX studies

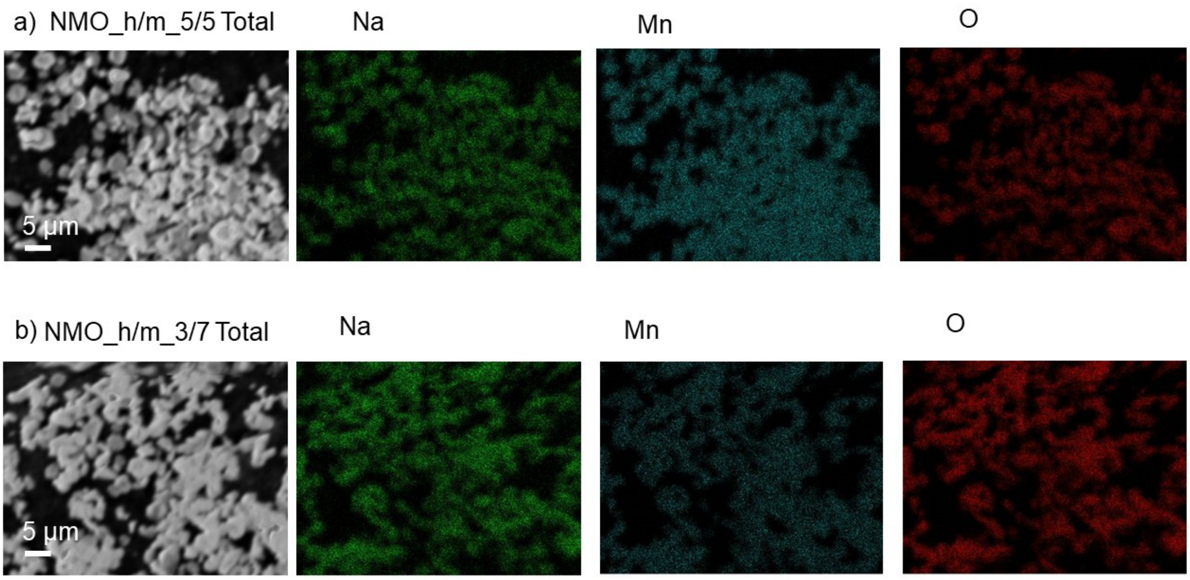

Figure S1. SEM/EDS maps of NMO powders: NMO_h/m_5/5 (a); NMO_h/m_3/7 (b).

Table S2. EDX signals gathered for 4 elements in the investigated NMO materials. The large contributions from oxygen and carbon come from signals from carbon tape.

EDX signals (%)			
Element	NMO_h_1	NMO_h/m_5/5	NMO_h/m_3/7
C	25.52	33.21	28.26
O	30.75	35.16	32.20
Na	9.18	6.64	8.30
Mn	34.55	24.99	31.24

The investigated materials were characterized using the SEM/EDX technique in order to identify, if any, inhomogeneous transition metal distribution and sodium aggregations. Images along with EDX signals are presented above. It can be seen that Na, Mn, and O elements are distributed evenly within the investigated grains.

Inductively Coupled Plasma-Optical Emission Spectrometry

Table S3: ICP-OES Composition Validation

Element	**NMO_h_1**	**NMO_h/m_5/5**	**NMO_h/m_3/7**
Na	0.60(4)	0.62(1)	0.61(2)
Mn	0.99(7)	1.02(2)	1.03(3)

Electrochemical performance

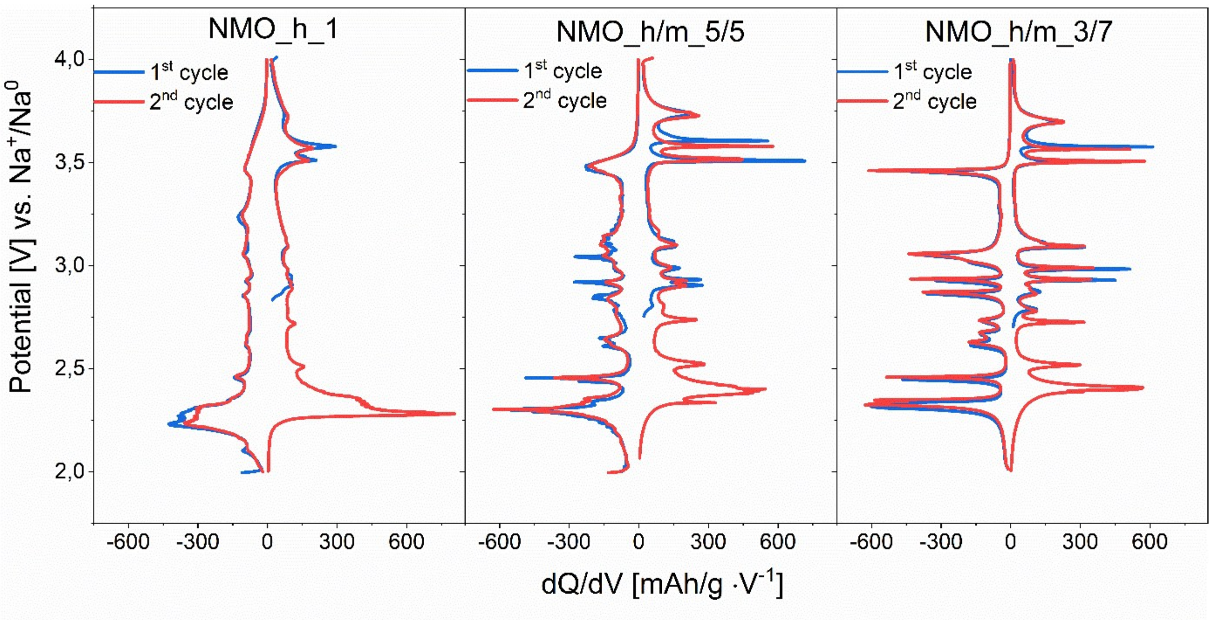

Figure S2. Comparison of the potential profiles as a function of dQ/dV during the 1st and 2nd cycle of charge/discharge processes for NMO_h_1 (a); NMO_h/m_5/5 (b); NMO_h/m_3/7 (c). Data recorded under C/20 current rate.

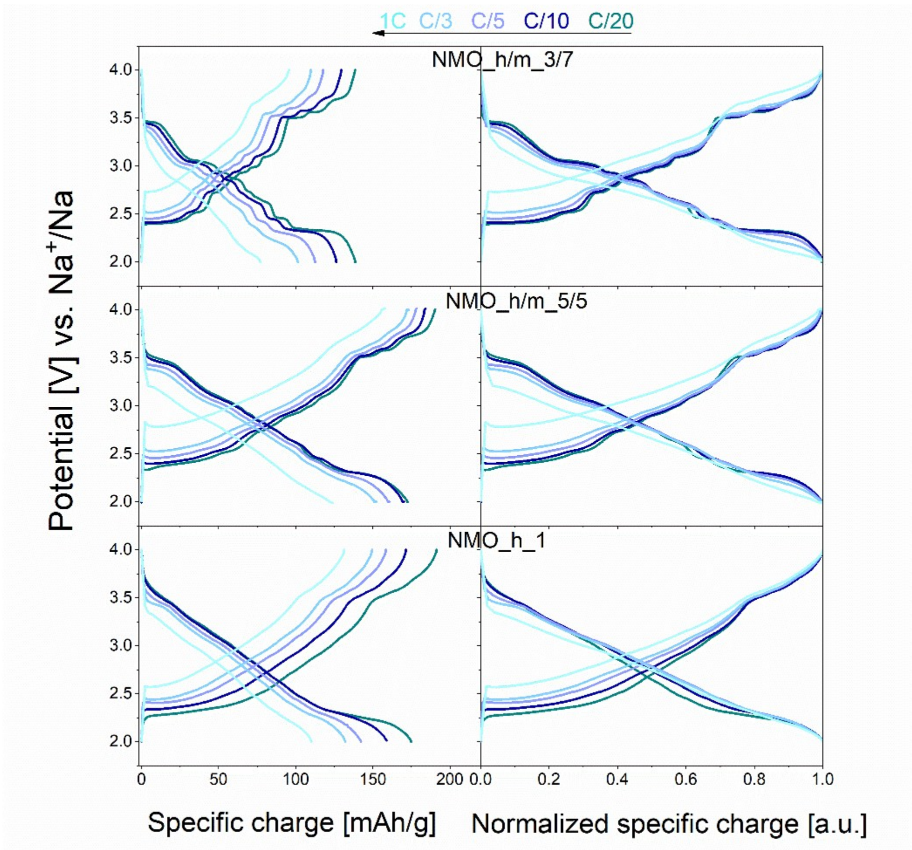

Figure S3. The charge/discharge potential profiles as a function of specific and normalized specific charge for the NMO samples recorded during rate capability tests. For the sake of comparison, only CC parts are shown.

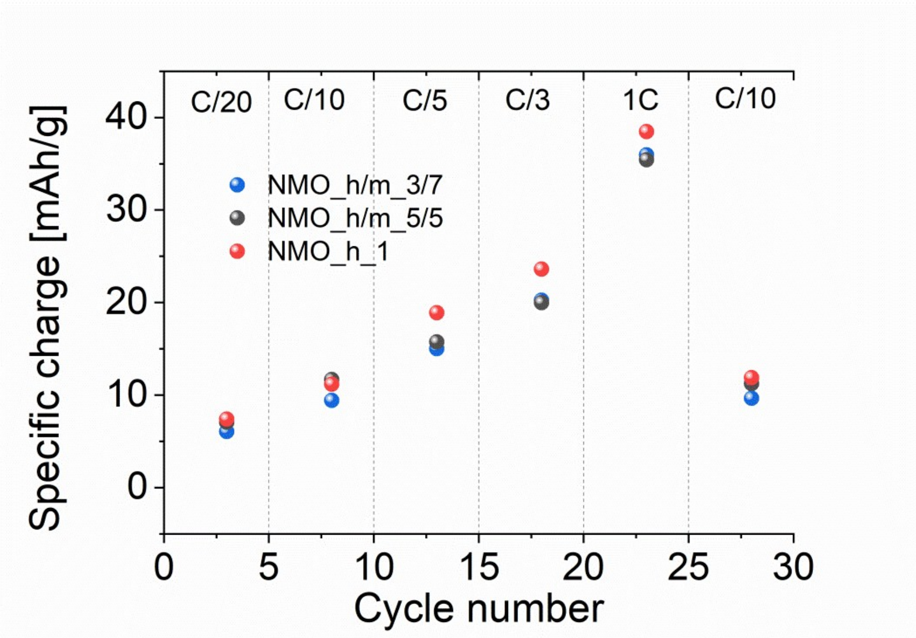

Figure S4. Specific charge obtained from the respective potentiostatic steps (during discharge) for investigated NMO electrodes during rate capability tests. For the sake of clarity only some specific values are presented.

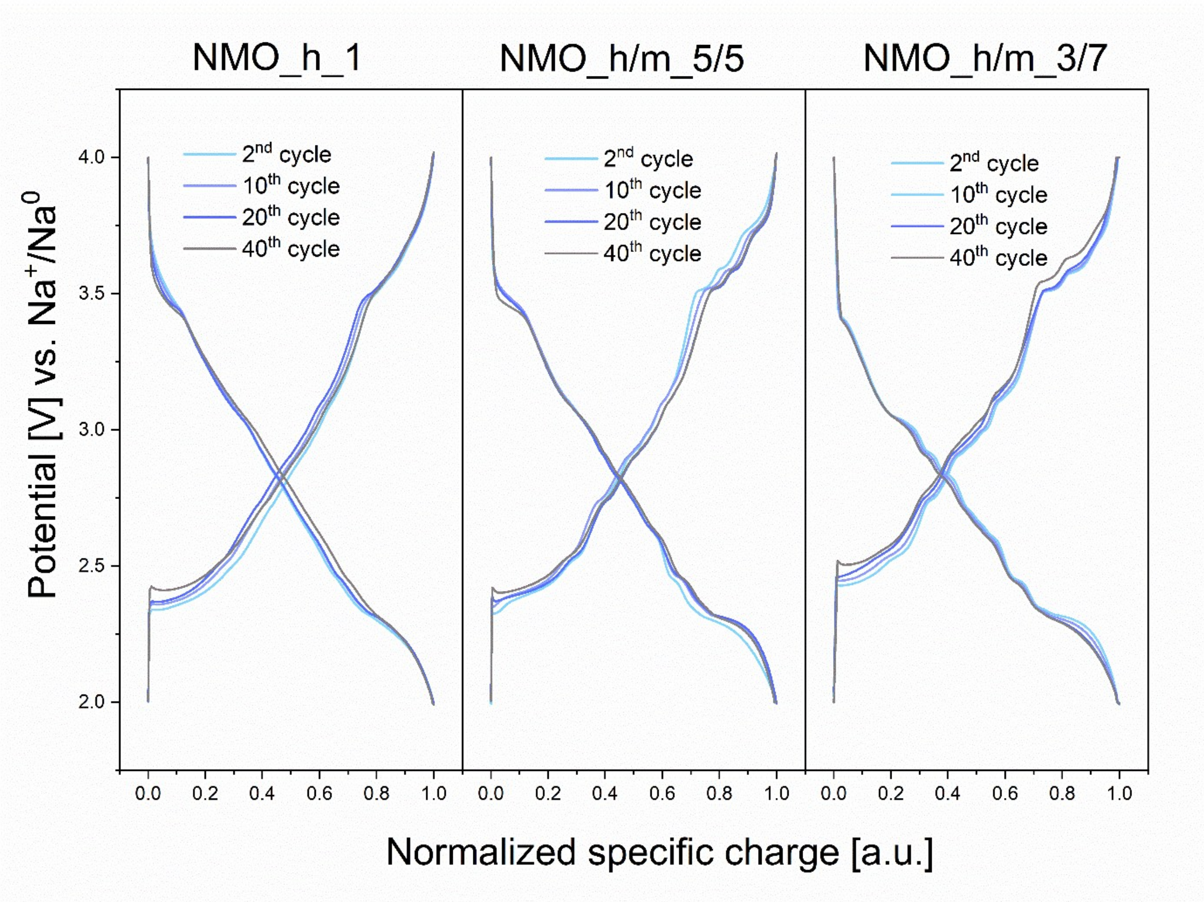

Figure S5. Potential profiles for 2nd, 10th, 20th and 40th cycles as a function of normalized specific charge of NMO samples. For the sake of comparison only CC parts are presented. Note that cycle 2-20 are registered under C/20 while 40th cycle under C/10 current rates.

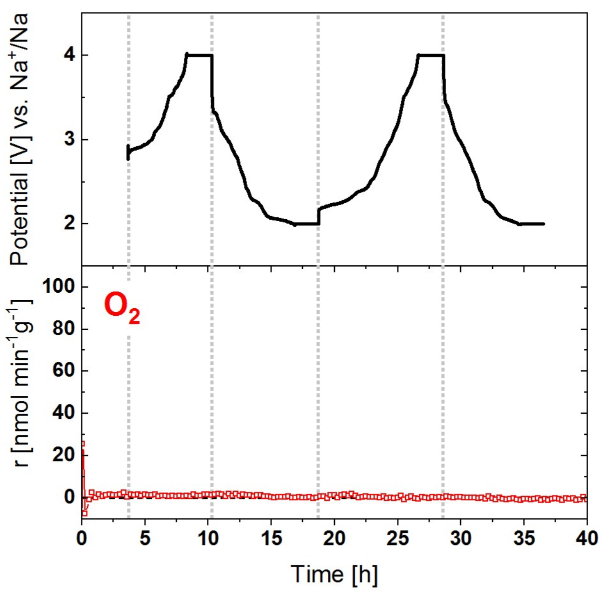

Figure S6. Online electrochemical mass spectrometry data for the NMO_h_1 sample.

Operando XRD studies first cycles

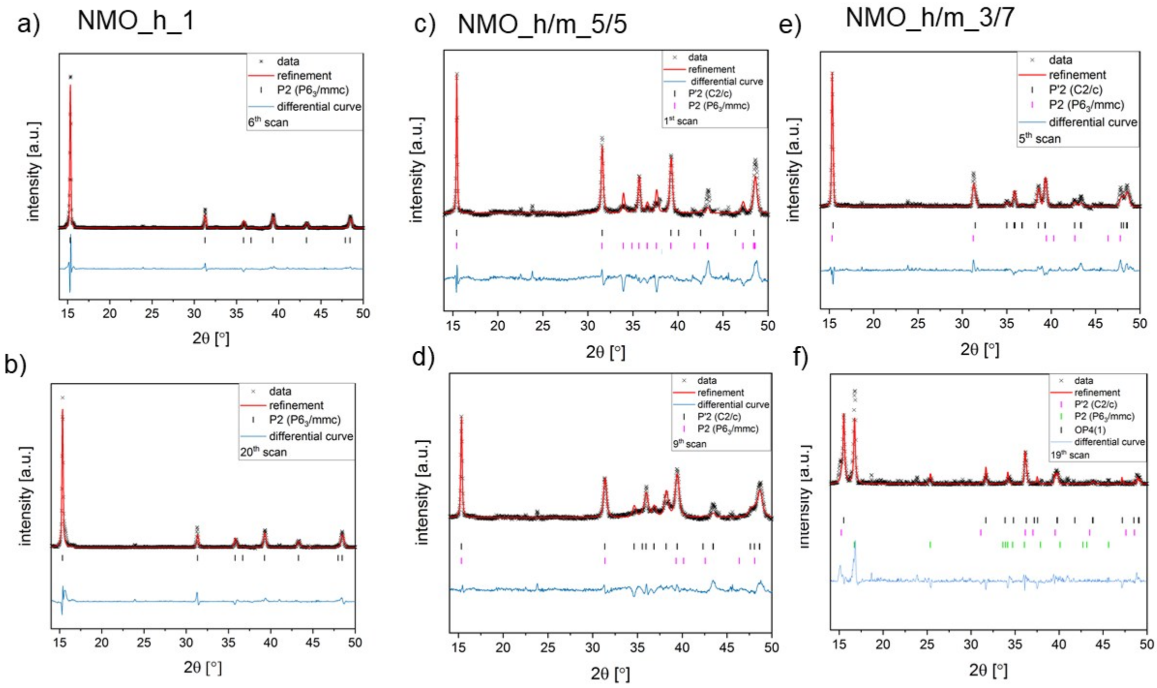

Figure S7. Selected _operando_ XRD patterns with Rietveld refinement for NMO samples: NMO_h_1 – 6th scan (a); NMO_h_1 – 20th scan (b); NMO_h/m_5/5 – 1st scan (c); NMO_h/m_5/5 – 9th scan (d); NMO_h/m_3/7 – 5th scan (e); NMO_h/m_3/7 – 19th scan (f).

Ex situ XAS studies

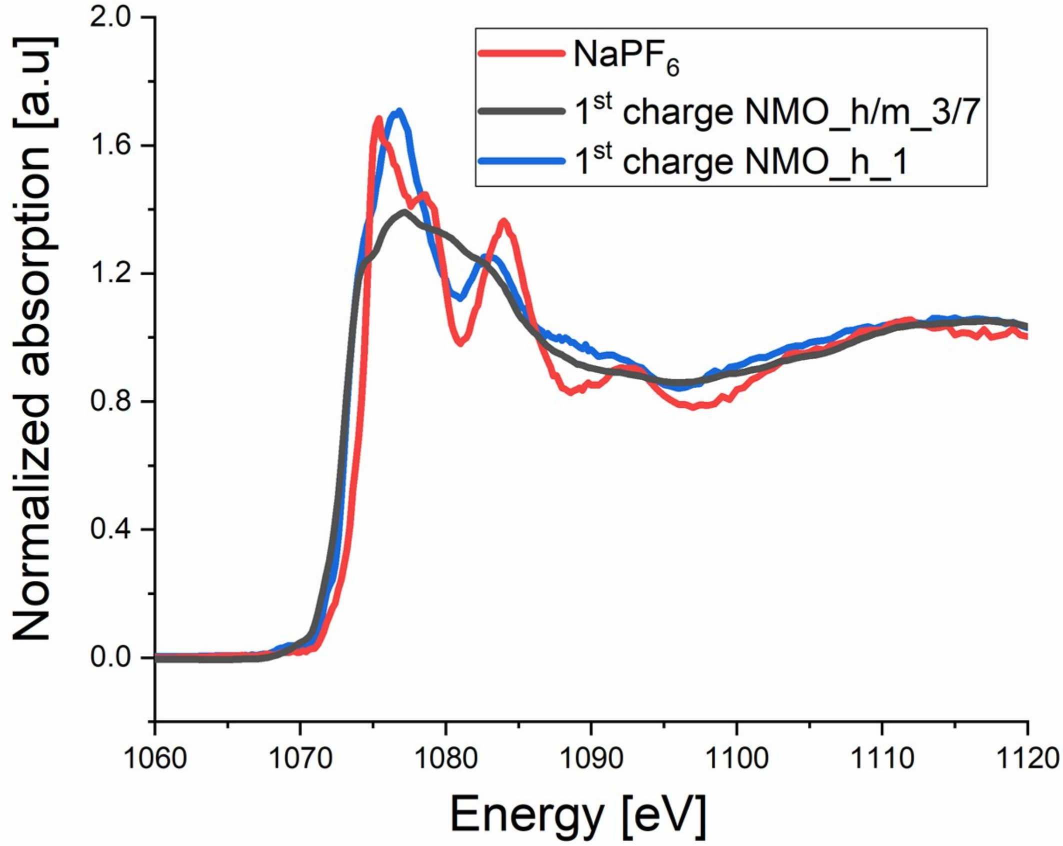

Figure S8. XAS spectra for $NaPF_6$ salt, NMO_h/m_3/7 charged to 4V and NMO_h_1 charged to 4V.