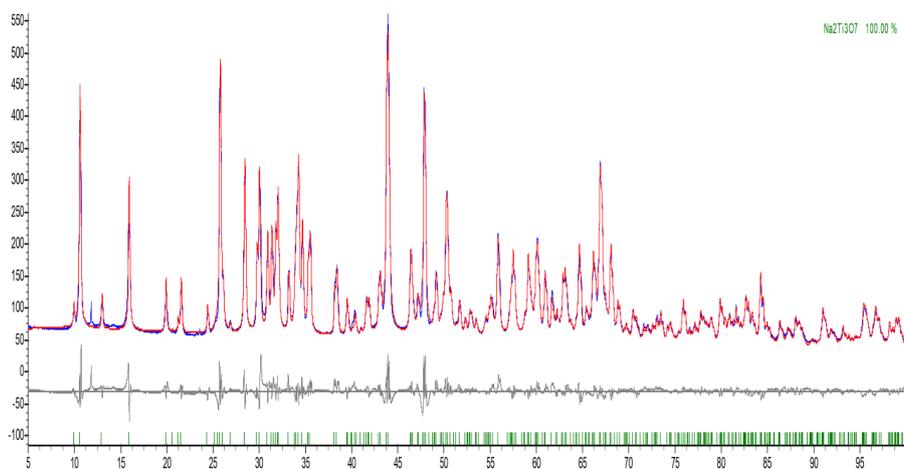


**Figure S1.** Rietveld refinement results of the X-ray powder diffraction pattern of  $\text{Na}_2\text{Ti}_3\text{O}_7$  (sample NTO-8h). Comparison of the experimental (—) and calculated (—) data.



**Figure S2.** Rietveld refinement results of the X-ray powder diffraction pattern of  $\text{Na}_2\text{Ti}_3\text{O}_7$  (sample NTO-48h). Comparison of the experimental (—) and calculated (—) data.

Supplementary Information of “Influence of the heat treatment duration on the cycling performance and electrochemical mechanism of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> as anode material for Na-ion batteries” by C. Piffet *et al.*

**Table S1.** Experimental details for the Rietveld refinements of the X-ray powder diffraction patterns of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>.

	<b>NTO-8h</b>	<b>NTO-48h</b>
<i>a</i> (Å)	9.1364(5)	9.1318(6)
<i>b</i> (Å)	3.8040(2)	3.8025(3)
<i>c</i> (Å)	8.5756(5)	8.5716(6)
$\beta$ (°)	101.590(2)	101.588(2)
<i>V</i> (Å <sup>3</sup> )	291.97(3)	291.57(3)
Space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>P</i> 2 <sub>1</sub> / <i>m</i>
<i>Z</i>	2	2
Absorption coefficient (cm <sup>-1</sup> )	30.9(15)	24.4(9)
Radiation (Å)	CuK $\alpha$ , 1.5418	CuK $\alpha$ , 1.5418
Temperature (K)	293(2)	293(2)
2 $\theta$ range (°)	5 - 100	5 - 100
Total no. of reflections	365	363
Refined parameters	51	51
Scale	1	1
Background	6	6
Zero, displacement, roughness	3	3
Absorption	1	1
FWHM, peak profile	4	4
Preferred orientations (111), (001)	3	3
Unit-cell parameters	4	4
Atom coordinates	24	24
Site occupancies	5	5
<i>R</i> <sub>Bragg</sub>	5.32	3.92
<i>R</i> <sub><i>p</i></sub>	10.52	9.20
<i>R</i> <sub><i>w</i><i>p</i></sub>	14.17	12.51
GOF	16.51	13.59

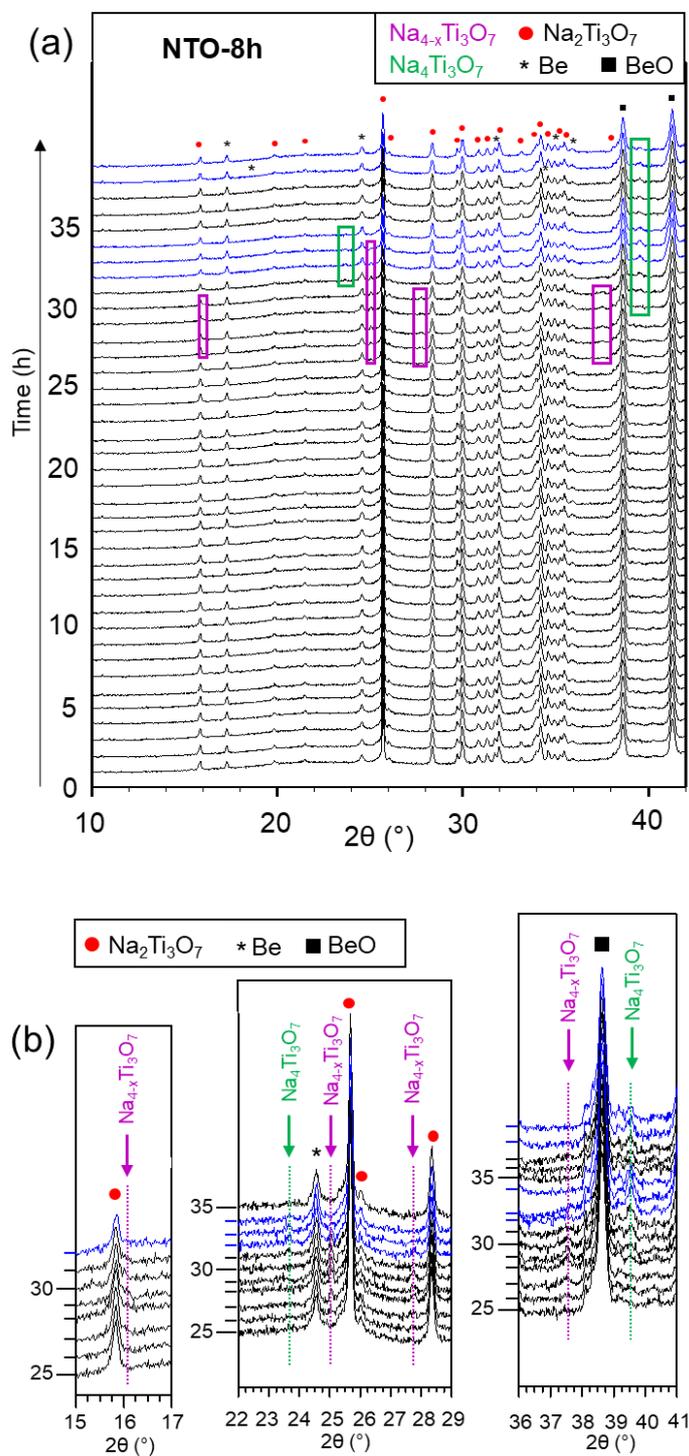
**Table S2.** Atom coordinates, isotropic temperature factors (Å<sup>2</sup>), and site occupancy factors for Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>.

	<b>NTO-8h</b>					<b>NTO-48h</b>				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>Biso</i>	<i>SOF</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>Biso</i>	<i>SOF</i>
Ti1	0.9837(4)	0.25	0.1443(5)	1	0.917(5)	0.9847(3)	0.25	0.1455(4)	1	0.961(5)
Ti2	0.6792(4)	0.25	0.2485(4)	1	0.976(6)	0.6790(3)	0.25	0.2480(3)	1	0.983(6)
Ti3	0.2811(4)	0.25	0.0305(4)	1	0.940(6)	0.2817(3)	0.25	0.0301(3)	1	0.961(5)
Na1	0.5939(8)	0.25	0.6799(9)	1	0.858(10)	0.5942(7)	0.25	0.6845(6)	1	0.949(9)
Na2	0.1533(9)	0.25	0.4933(10)	1	0.778(9)	0.1552(8)	0.25	0.5018(8)	1	0.899(8)
O1	0.1841(12)	0.25	0.2176(14)	1	1	0.1835(10)	0.25	0.2171(10)	1	1
O2	0.4678(12)	0.25	0.1464(15)	1	1	0.4642(10)	0.25	0.1401(11)	1	1
O3	0.6440(12)	0.25	0.4431(12)	1	1	0.6439(10)	0.25	0.4477(10)	1	1
O4	0.9026(12)	0.25	0.3201(14)	1	1	0.9075(9)	0.25	0.3242(10)	1	1
O5	0.7517(12)	0.25	0.0164(17)	1	1	0.7518(10)	0.25	0.0182(11)	1	1
O6	0.3188(12)	0.25	0.7904(15)	1	1	0.3226(10)	0.25	0.8102(11)	1	1
O7	0.0417(13)	0.25	0.9112(14)	1	1	0.0381(10)	0.25	0.9156(10)	1	1

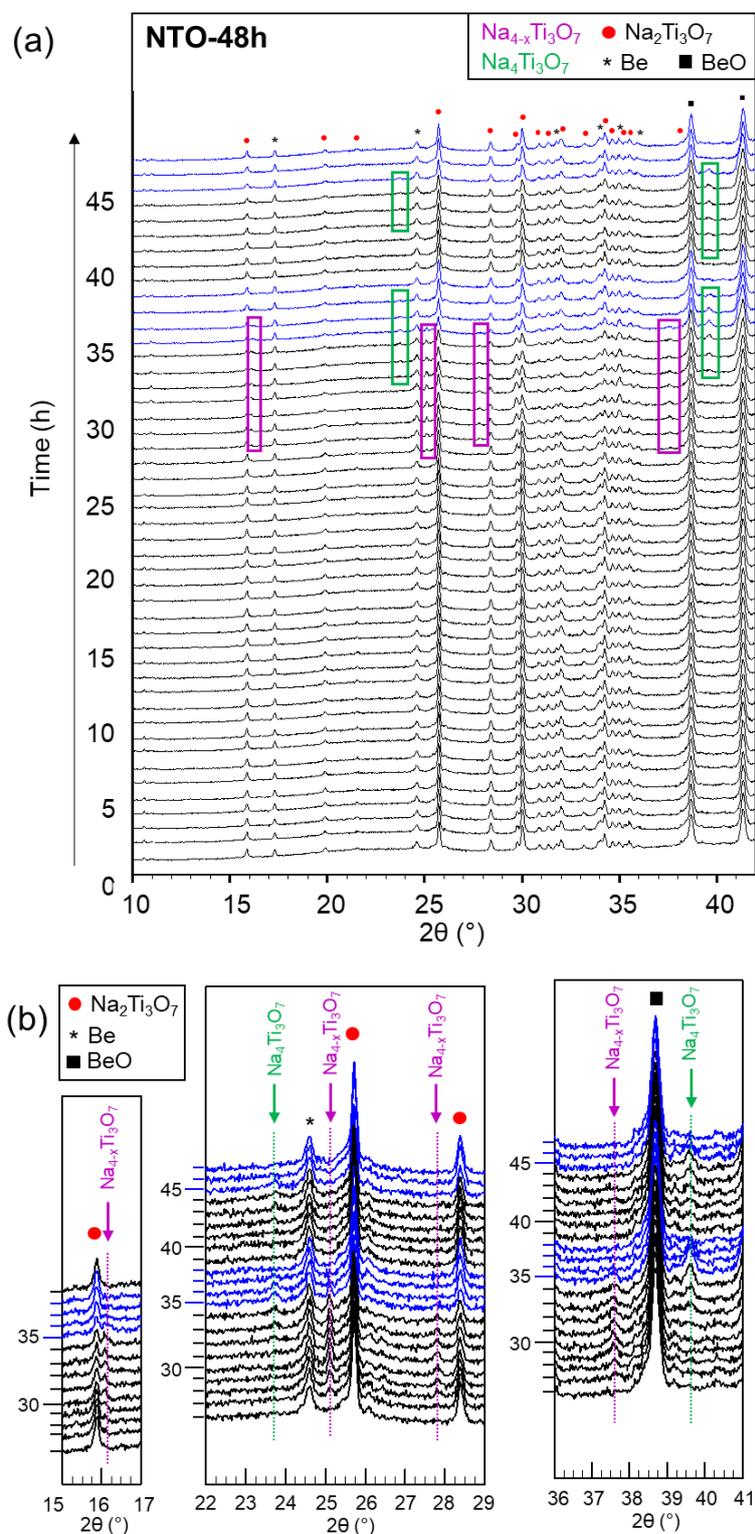
Supplementary Information of “Influence of the heat treatment duration on the cycling performance and electrochemical mechanism of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> as anode material for Na-ion batteries” by C. Piffet *et al.*

**Table S3.** Selected interatomic distances (Å), bond-length distortion parameters (BLD, %), and bond valence sums (BVS, valence units) for the crystal structure of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>.

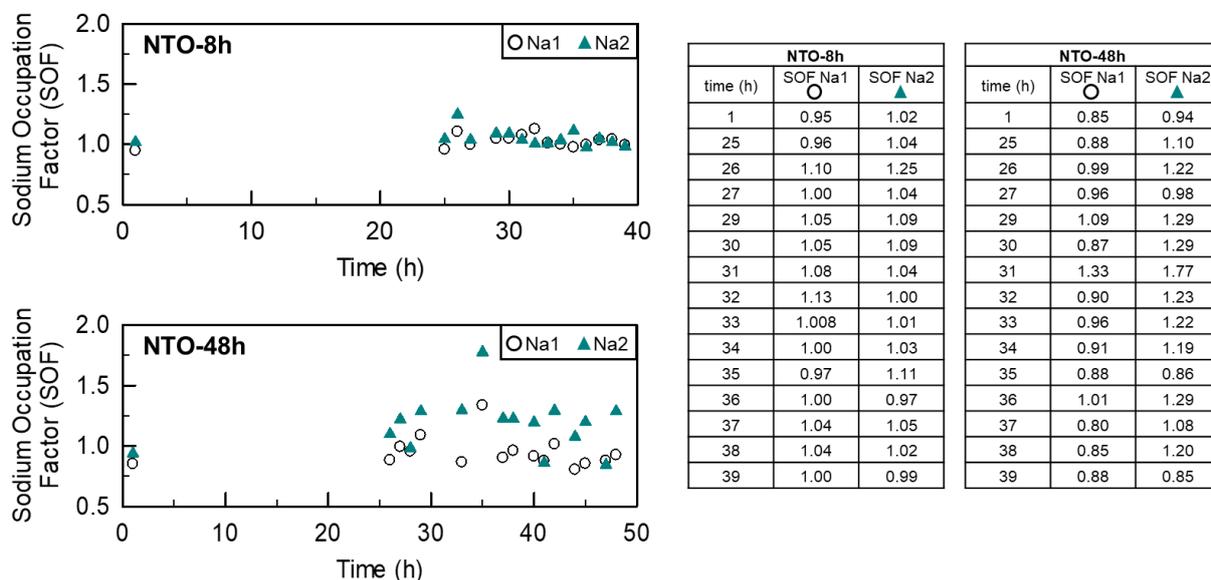
	<b>NTO-8h</b>	<b>NTO-48h</b>		<b>NTO-8h</b>	<b>NTO-48h</b>
Ti1-O4	1.809(14)	1.810(13)	Na1-O3	2.170(14)	2.167(14)
Ti1-O1	1.812(12)	1.796(10)	Na1-O2	2.548(11) x 2	2.546(11) x 2
Ti1-O7	1.963(3) x 2	1.972(3) x 2	Na1-O1	2.791(10) x 2	2.786(8) x 2
Ti1-O7	2.168(14)	2.123(11)	Na1-O6	2.859(15)	2.896(14)
Ti1-O5	2.182(12)	2.187(10)	Na1-O3	2.921(10) x 2	2.939(8) x 2
<Ti1-O>	1.983	1.977	Na1-O5	2.955(15)	2.932(15)
BLD	6.467	6.012	<Na1-O>	2.723	2.726
BVS	4.12	4.18	BLD	7.366	7.497
			BVS	0.98	0.97
Ti2-O3	1.762(12)	1.804(12)			
Ti2-O6	1.932(3) x 2	1.965(4) x 2	Na2-O1	2.436(16)	2.505(16)
Ti2-O2	1.954(11)	1.994(10)	Na2-O4	2.467(13)	2.460(11)
Ti2-O4	2.010(12)	2.057(9)	Na2-O4	2.601(11) x 2	2.551(11) x 2
Ti2-O5	2.220(16)	2.202(16)	Na2-O3	2.634(10) x 2	2.617(8) x 2
<Ti2-O>	1.968	1.998	Na2-O6	2.689(14)	2.775(14)
BLD	4.975	4.402	<Na2-O>	2.581	2.582
BVS	4.22	3.85	BLD	2.852	2.897
			BVS	0.88	0.88
Ti3-O2	1.793(11)	1.742(10)			
Ti3-O5	1.955(3) x 2	1.957(3) x 2			
Ti3-O1	1.983(14)	1.988(13)			
Ti3-O6	2.155(14)	1.994(14)			
Ti3-O7	2.221(12)	2.244(9)			
<Ti3-O>	2.010	1.980			
BLD	5.890	4.794			
BVS	3.80	4.14			



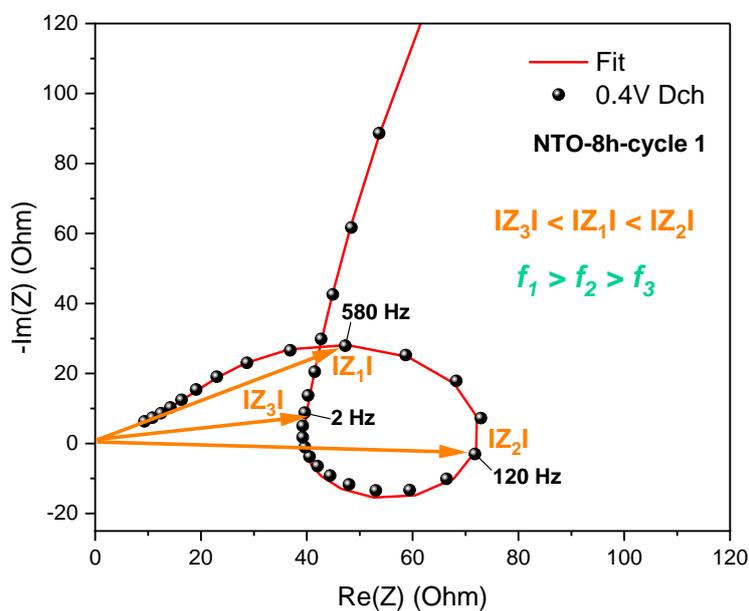
**Figure S3.** *Operando* electrochemical XRD patterns of  $\text{Na}_2\text{Ti}_3\text{O}_7$  heat treated at  $800^\circ\text{C}$  for 8h (NTO-8h). Each diffractogram is recorded in 1 h. Cycling rate: C/20. Black curves for data recorded during discharge and blue curves during charge.



**Figure S4.** Operando electrochemical XRD patterns of  $\text{Na}_2\text{Ti}_3\text{O}_7$  heat treated at  $800^\circ\text{C}$  for 48h (NTO-48h). Each diffractogram is recorded in 1 h. Cycling rate: C/20. Black curves for data recorded during discharge and blue curves during charge.

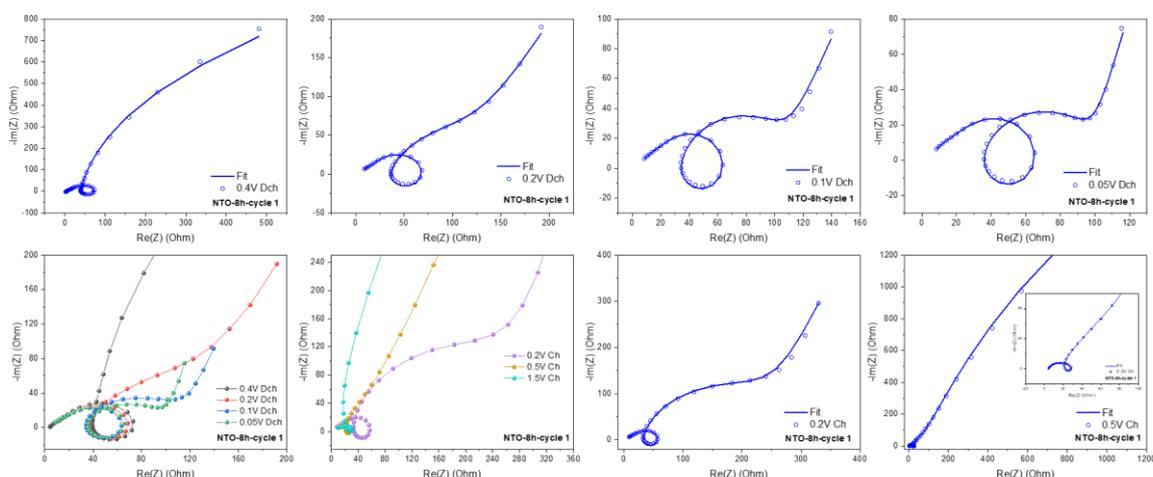


**Figure S5.** Site Occupation Factors (SOF) for Na1 and Na2 sites calculated from Rietveld refinement of *operando* XRD patterns (Figure S4 and S5) of  $\text{Na}_2\text{Ti}_3\text{O}_7$  heat treated at  $800^\circ\text{C}$  for 8 h (NTO-8h) or 48 h (NTO-48h).

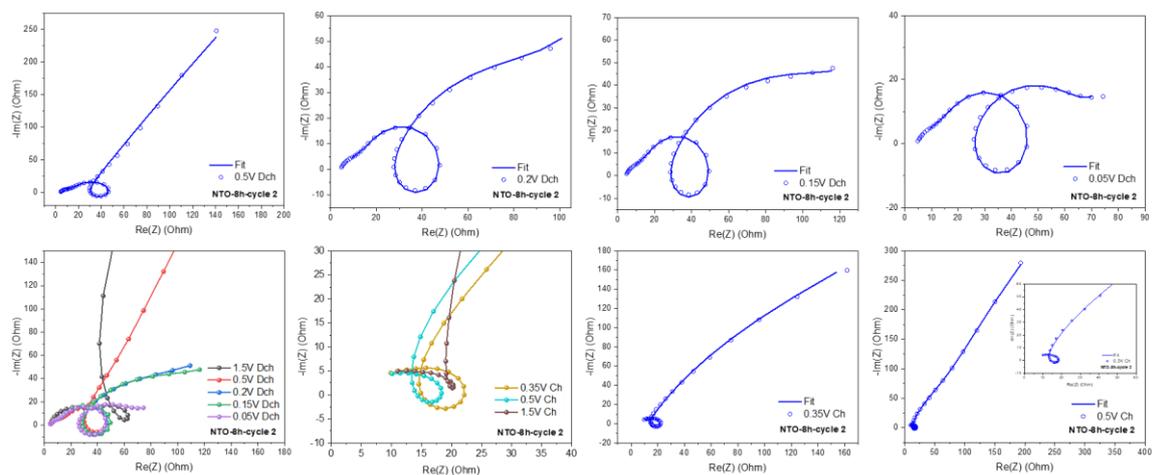


**Figure S6.** Frequency dependency in the Nyquist plot for the inductive loop of NTO-8h at 0.4V in the first discharge.

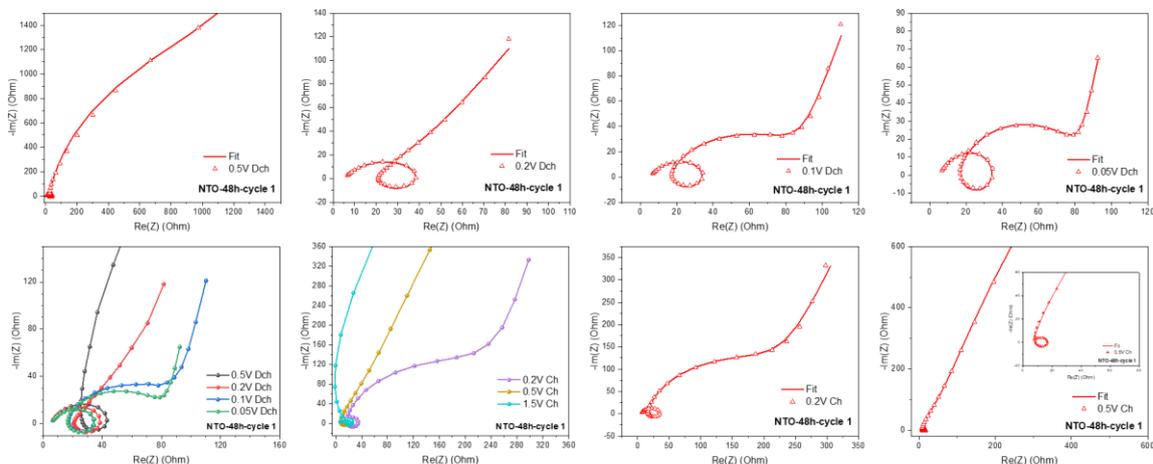
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**Figure S7.** Nyquist plots of NTO-8h at different voltage steps in the first cycle where solid line shows fit to the experimental data.

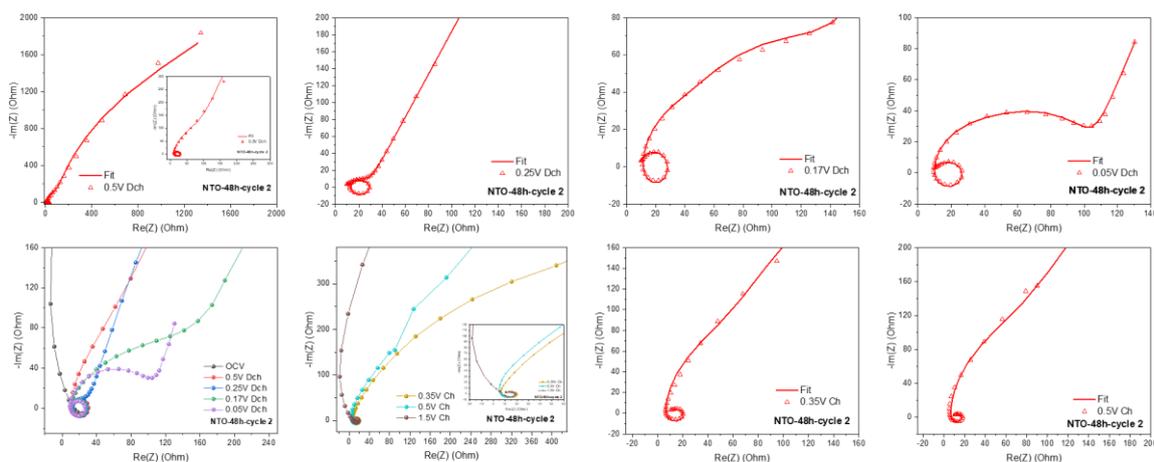


**Figure S8.** Nyquist plots of NTO-8h at different voltage steps in the second cycle where solid line shows fit to the experimental data.

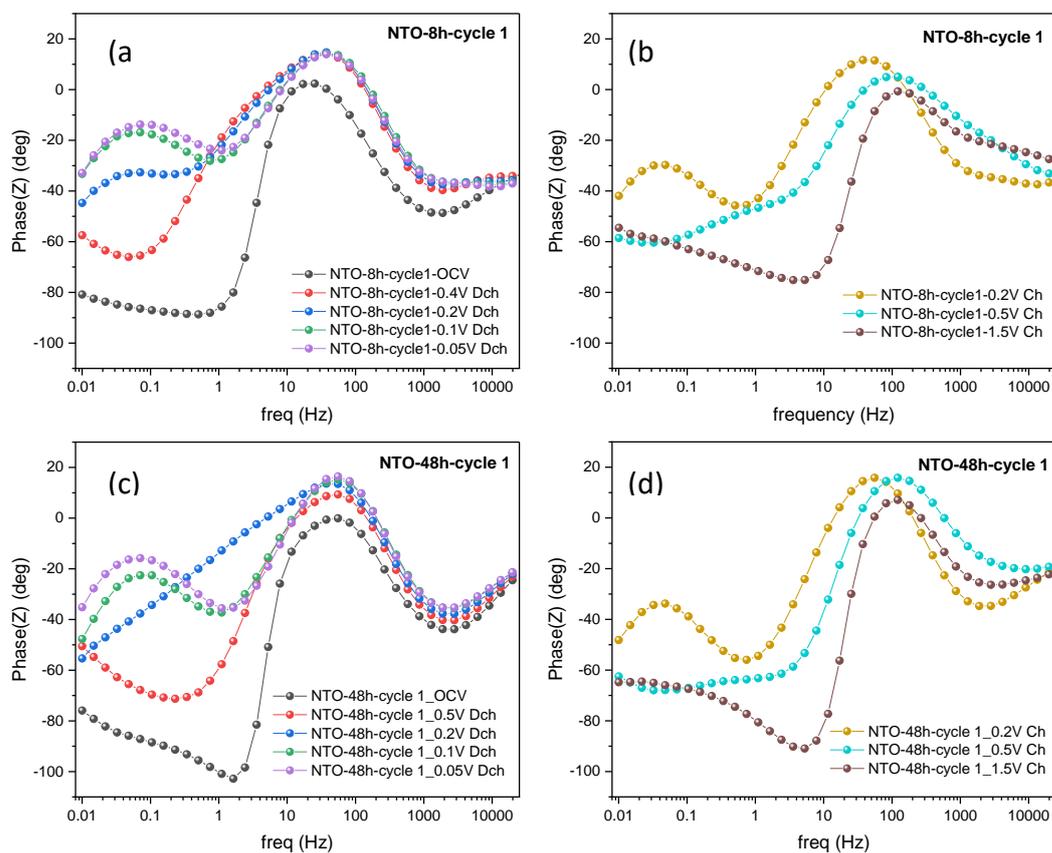


**Figure S9.** Nyquist plots of NTO-48h at different voltage steps in the first cycle where solid line shows fit to the experimental data.

Supplementary Information of “Influence of the heat treatment duration on the cycling performance and electrochemical mechanism of  $\text{Na}_2\text{Ti}_3\text{O}_7$  as anode material for Na-ion batteries” by C. Piffet *et al.*



**Figure S10.** Nyquist plots of NTO-48h at different voltage steps in the second cycle where solid line shows fit to the experimental data.



**Figure S11.** Bode plots of (a,b) NTO-8h and (c,d) NTO-48h showing the phase angle–frequency dependence at different voltage steps in the discharge and charge steps of the first cycle.

Supplementary Information of “Influence of the heat treatment duration on the cycling performance and electrochemical mechanism of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> as anode material for Na-ion batteries” by C. Piffet *et al.*

**Table S4.** Impedance parameters derived using equivalent circuit models of NTO-8h and NTO-48h.

NTO-08h-cycle 01						
	R <sub>s</sub>	R <sub>SEI</sub>	R <sub>ct</sub>	R <sub>L'</sub>	R <sub>L''</sub>	χ <sup>2</sup>
0.40V dch	4.67619	19.7898	848.579	50.1811	20.0434	0.01453
0.20V dch	4.25	20.7399	74.6321	44.3964	11.5414	0.02404
0.10V dch	3.84252	24.2214	71.0775	36.9972	4.92532	0.02045
0.05V dch	4.25	24.5598	63.4911	37.8714	5.29256	0.01546
0.20V ch	4.17746	23.3757	202.619	30.738	2.78668	0.02941
0.50V ch	3.64916	52.8194	7752.19	26.0022	26.9752	0.01787
NTO-08h-cycle 02						
	R <sub>s</sub>	R <sub>SEI</sub>	R <sub>ct</sub>	R <sub>L'</sub>	R <sub>L''</sub>	χ <sup>2</sup>
0.50V dch	3.26341	18.8977	11047.5	25.3132	4.30945	0.01136
0.20V dch	4.27575	16.3511	72.7803	28.0812	5.44542	0.01323
0.15V dch	4.60264	15.8627	90.4327	29.4972	4.65503	0.00983
0.05V dch	4.68567	14.6566	38.6455	27.3855	4.66022	0.01191
0.35V ch	4.97512	6.60894	213.432	10.0102	3.011	0.03111
0.50V ch	4.5468	85.9209	1048.28	13.7408	9.62488	0.03787
1.50V ch	4.92549	192.376	1186.09	16.5434	45.1806	0.01052
NTO-48h-cycle 01						
	R <sub>s</sub>	R <sub>SEI</sub>	R <sub>ct</sub>	R <sub>L'</sub>	R <sub>L''</sub>	χ <sup>2</sup>
0.50V dch	5.60845	10.5131	1664.08	28.0239	12.5171	0.0738
0.20V dch	5.66161	13.6953	14.7978	20.136	1.05082	0.01962
0.10V dch	5.60601	7.91952	69.0698	21.0352	2.98872	0.02251
0.05V dch	5.68916	7.4287	66.7178	21.7708	2.17598	0.02058
0.20V ch	5.70372	9.58225	193.577	19.8088	0.01394	0.02718
0.50V ch	6.23521	29.9245	7609.2	10.7844	0.38207	0.08213
NTO-48h-cycle 02						
	R <sub>s</sub>	R <sub>SEI</sub>	R <sub>ct</sub>	R <sub>L'</sub>	R <sub>L''</sub>	χ <sup>2</sup>
0.50V dch	8.46695	73.8512	2149.68	23.4028	2.41528	0.08614
0.25V dch	7.95773	1.08605	16.262	22.2896	2.656	0.03892
0.17V dch	8.30361	27.8018	91.0257	22.2968	2.10028	0.04466
0.05V dch	8.08578	37.2114	53.2113	21.2632	1.18522	0.0345
0.35V ch	4.23467	508.216	55.7638	20.6499	2.28398	0.20115
0.50V ch	5.46881	464.893	90.5206	13.6628	1.10005	0.46041