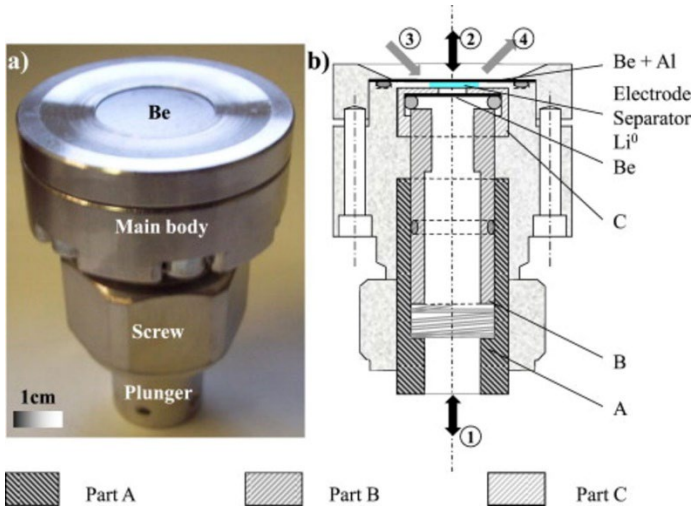


Figure S1. Electrochemical cell for operando measurements. (a) Photo and (b) Scheme of the device. From Leriche *et al.* [30]

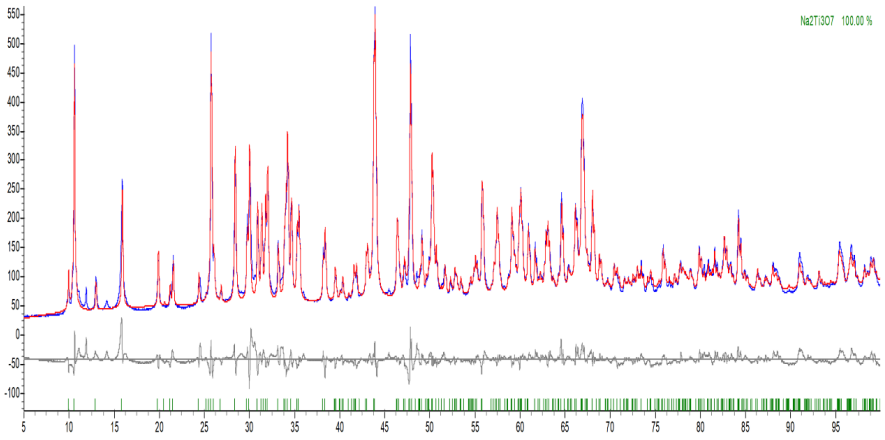


Figure S2. Rietveld refinnement results of the X-ray powder diffraction pattern of $Na_2Ti_3O_7$ (sample NTO-8h). Comparison of the experimental (▬) and calculated (—) data.

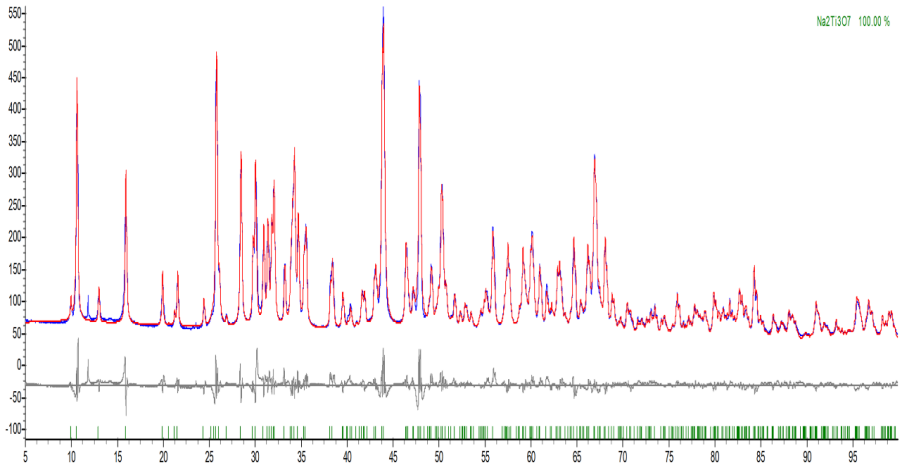


Figure S3. Rietveld refinnement results of the X-ray powder diffraction pattern of $Na_2Ti_3O_7$ (sample NTO-48h). Comparison of the experimental (▬) and calculated (—) data.

Table S1. Experimental details for the Rietveld refinements of the X-ray powder diffraction patterns of $Na_2Ti_3O_7$.

	NTO-8h	**NTO-48h**
a (Å)	9.1364(5)	9.1318(6)
b (Å)	3.8040(2)	3.8025(3)
c (Å)	8.5756(5)	8.5716(6)
β (°)	101.590(2)	101.588(2)
V (Å^3)	291.97(3)	291.57(3)
Space group	$P2_1/m$	$P2_1/m$
Z	2	2
Absorption coefficient (cm^{-1})	30.9(15)	24.4(9)
Radiation (Å)	CuK_α, 1.5418	CuK_α, 1.5418
Temperature (K)	293(2)	293(2)
2θ 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
R_{Bragg}	5.32	3.92
R_p	10.52	9.20
R_{wp}	14.17	12.51
GOF	16.51	13.59

Table S2. Atom coordinates, isotropic temperature factors (Å^2), and site occupancy factors for $Na_2Ti_3O_7$.

	NTO-8h					**NTO-48h**				
	x	*y*	*z*	*Biso*	*SOF*	*x*	*y*	*z*	*Biso*	*SOF*
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

Table S3. Selected interatomic distances (Å), bond-length distortion parameters (BLD, %), and bond valence sums (BVS, valence units) for the crystal structure of $Na_2Ti_3O_7$.

	NTO-8h	**NTO-48h**		**NTO-8h**	**NTO-48h**
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			

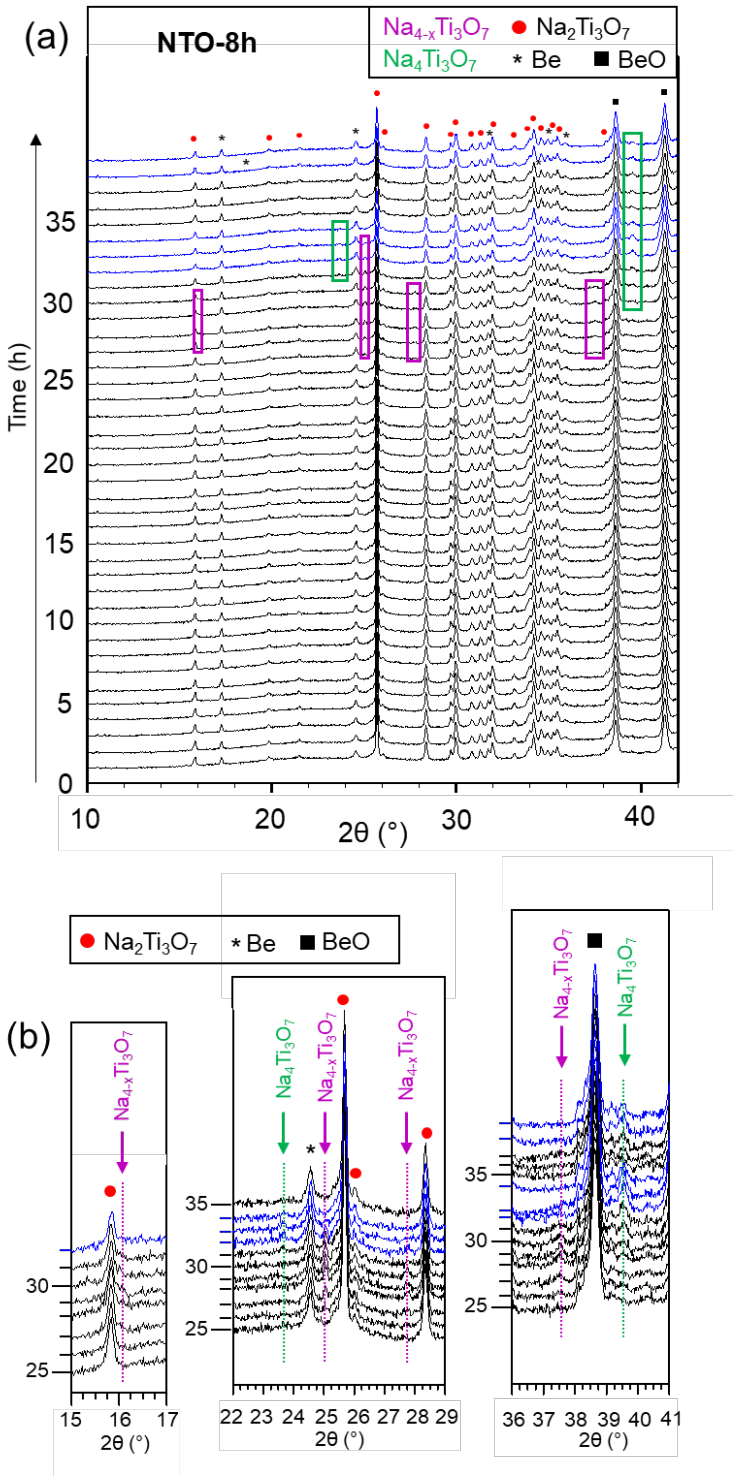


Figure S4. *Operando* electrochemical XRD patterns of $Na_2T_3O_7$ heat treated at 800°C for 8h (NTO-8h). Each diffractogram is recorded in 1 h. Cycling rate: C/20. Black curves for data recorded during discharge and blue curves during charge.

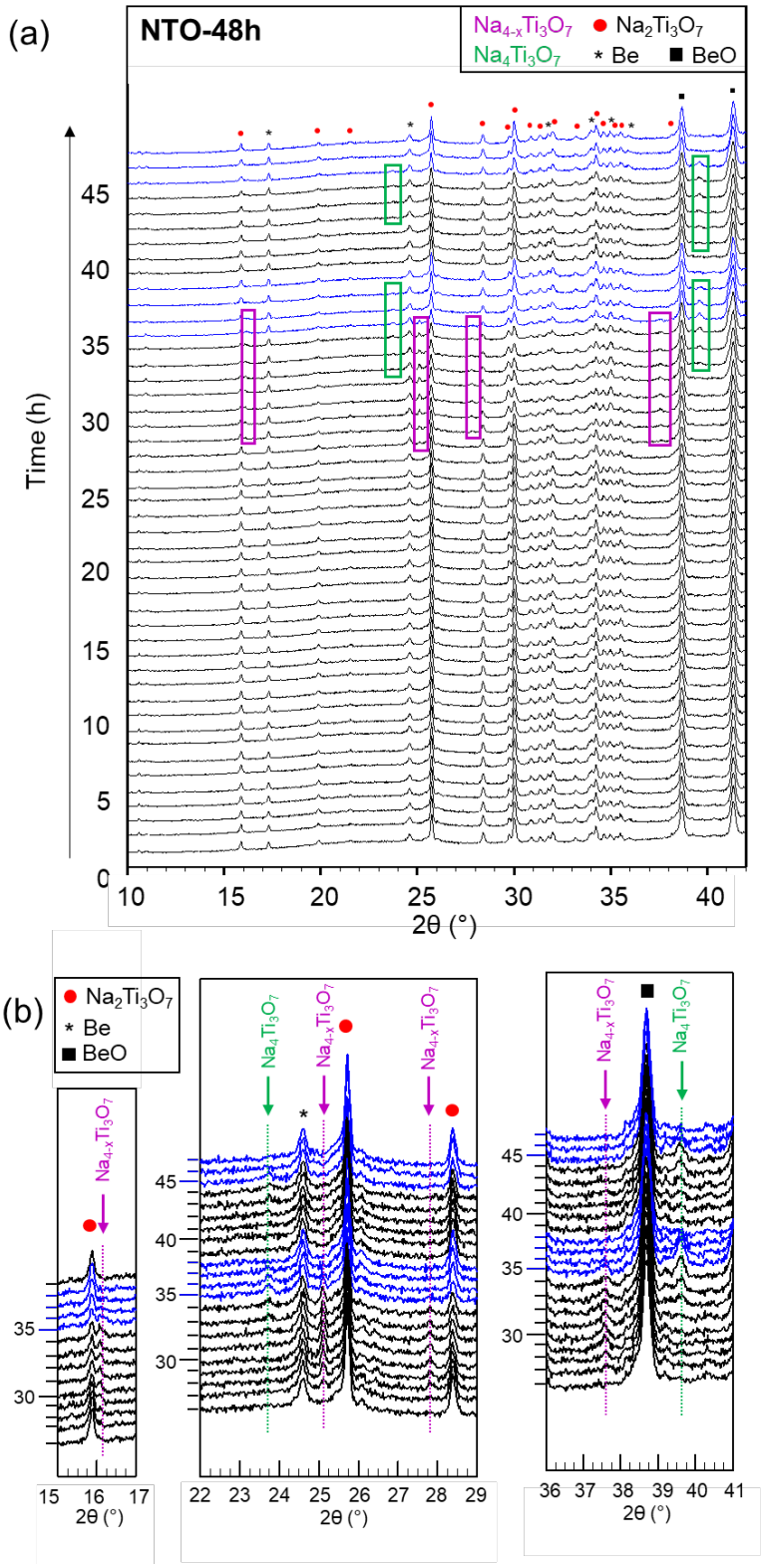
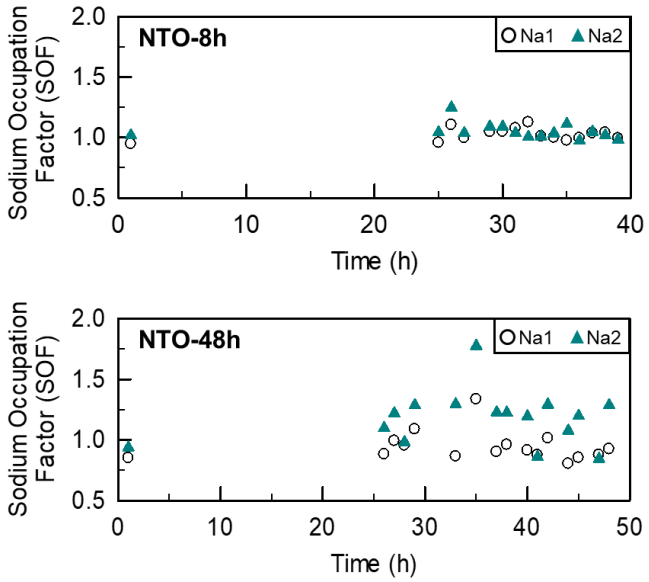


Figure S5. *Operando* electrochemical XRD patterns of $Na_2T_3O_7$ heat treated at 800°C for 48h (NTO-48h). Each diffractogram is recorded in 1 h. Cycling rate: C/20. Black curves for data recorded during discharge and blue curves during charge.



NTO-8h		
time (h)	SOF Na1 ○	SOF Na2 ▲
1	0.95	1.02
25	0.96	1.04
26	1.10	1.25
27	1.00	1.04
29	1.05	1.09
30	1.05	1.09
31	1.08	1.04
32	1.13	1.00
33	1.008	1.01
34	1.00	1.03
35	0.97	1.11
36	1.00	0.97
37	1.04	1.05
38	1.04	1.02
39	1.00	0.99

NTO-48h		
time (h)	SOF Na1 ○	SOF Na2 ▲
1	0.85	0.94
25	0.88	1.10
26	0.99	1.22
27	0.96	0.98
29	1.09	1.29
30	0.87	1.29
31	1.33	1.77
32	0.90	1.23
33	0.96	1.22
34	0.91	1.19
35	0.88	0.86
36	1.01	1.29
37	0.80	1.08
38	0.85	1.20
39	0.88	0.85

Figure S6. Site Occupation Factors (SOF) for Na1 and Na2 sites calculated from Rietveld refinement of *operando* XRD patterns (Figure S4 and S5) of $Na_2T_3O_7$ heat treated at 800°C for 8 h (NTO-8h) or 48 h (NTO-48h).

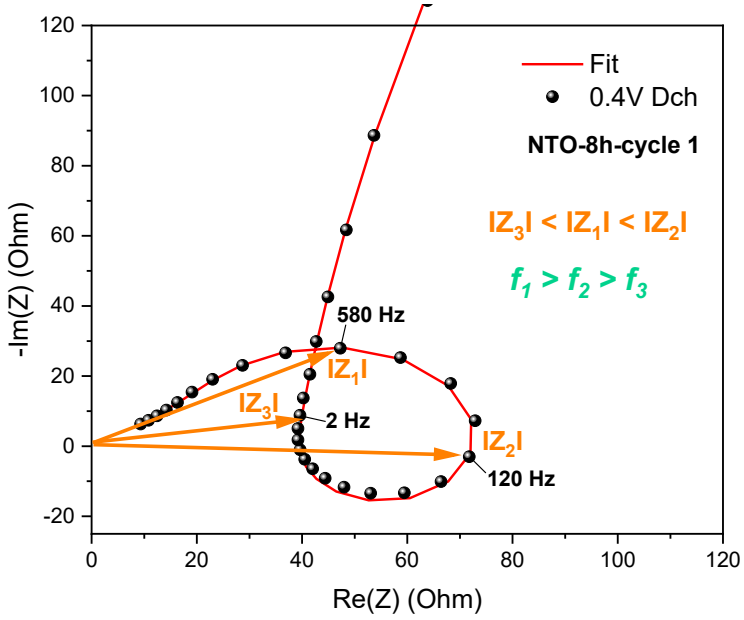


Figure S7. Frequency dependency in the Nyquist plot for the inductive loop of NTO-8h at 0.4V in the first discharge.

As shown in figure S7, the impedance (|Z|) evolution does not follow the inverse dependency as it should. As the frequency decreases $f_1>f_2>f_3$ the impedance response, $|Z_3|<|Z_1|<|Z_2|$ only increases up to the second point at 120 Hz and then decreases at 2 Hz. Before further analysing the loop, we clarified that this feature is not a measurement artifact and checked the EIS data accuracy and validity. The easiest way to check this was to perform Kramers-Kronig test, a powerful tool to identify artifacts errors in a spectrum, which are mathematical relations for the real and imaginary components of a complex system that define it as linear, causal, stable, and

finite. There is an excellent correlation between experimental results and the Kramers-Kronig fit with a $\chi 2$ error statistic of only 0.003-0.005, showing no drift. As a result, the loop in the impedance spectra will have to be represented geometrically in the equivalent circuit.

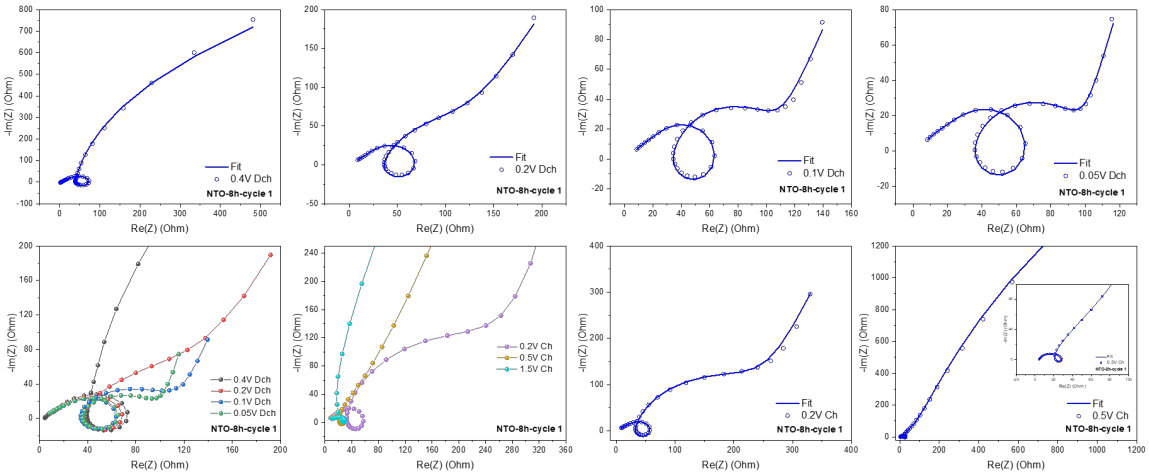


Figure S8. Nyquist plots of NTO-8h at different voltage steps in the first cycle where dot line shows the experimental and solid line fitting results.

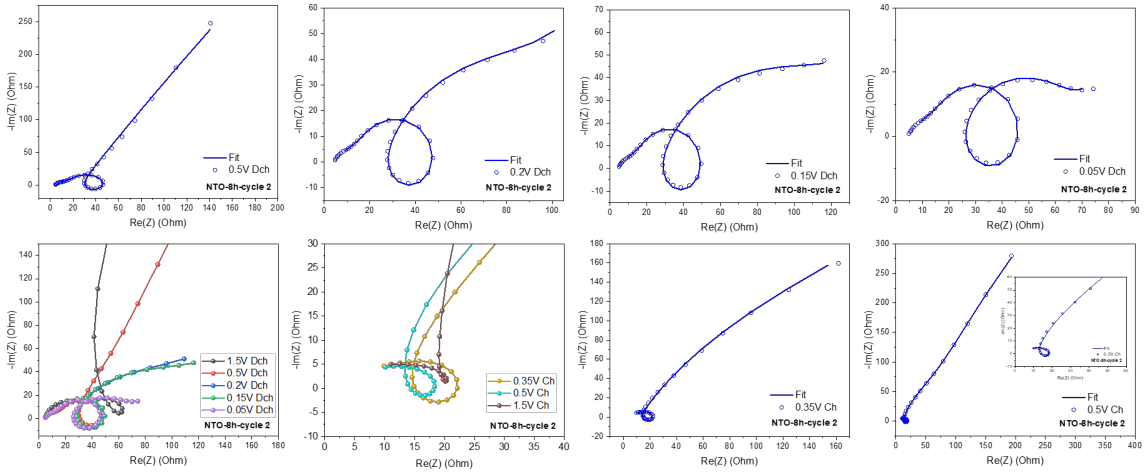


Figure S9. Nyquist plots of NTO-8h at different voltage steps in the second cycle where dot line shows the experimental and solid line fitting results.

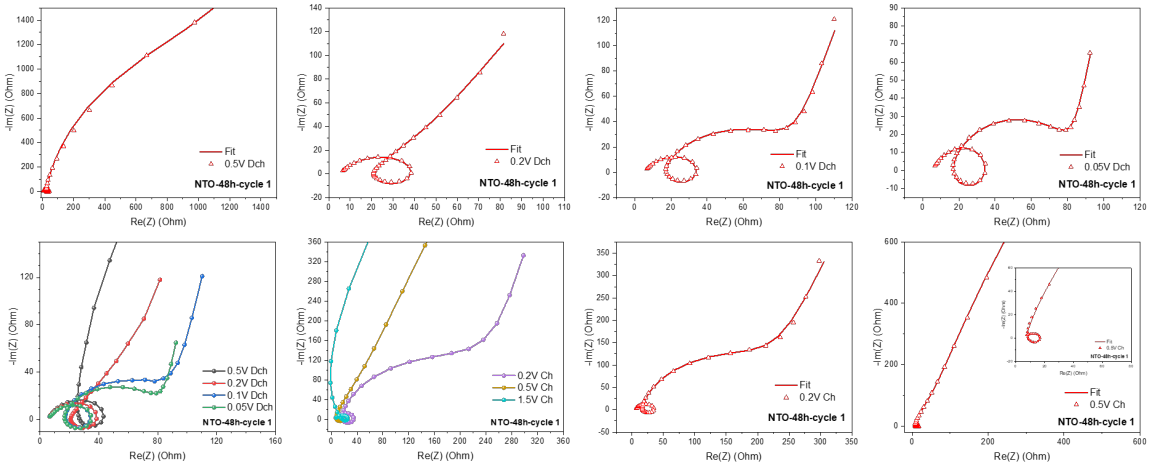


Figure S10. Nyquist plots of NTO-48h at different voltage steps in the first cycle where dot line shows the experimental and solid line fitting results.

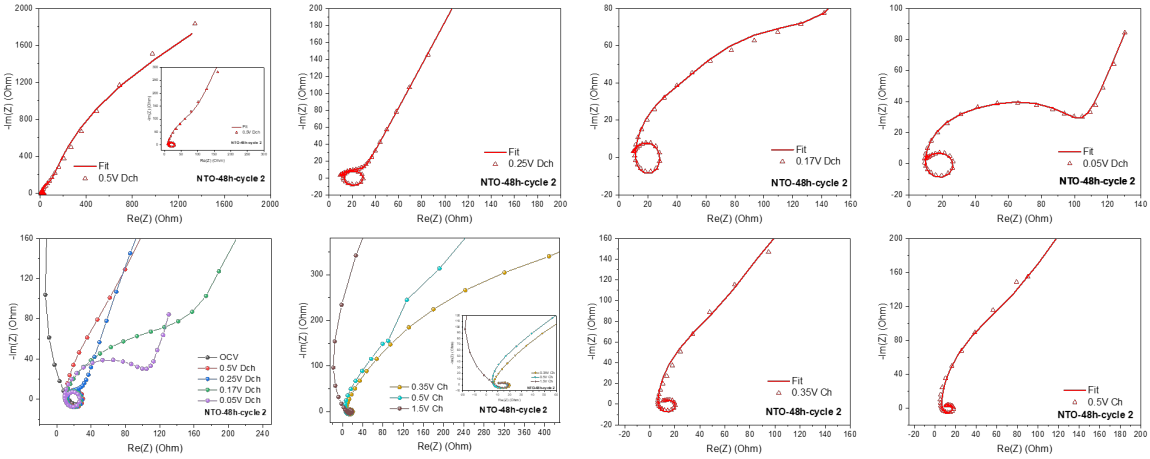


Figure S11. Nyquist plots of NTO-48h at different voltage steps in the second cycle where dot line shows the experimental and solid line fitting results.

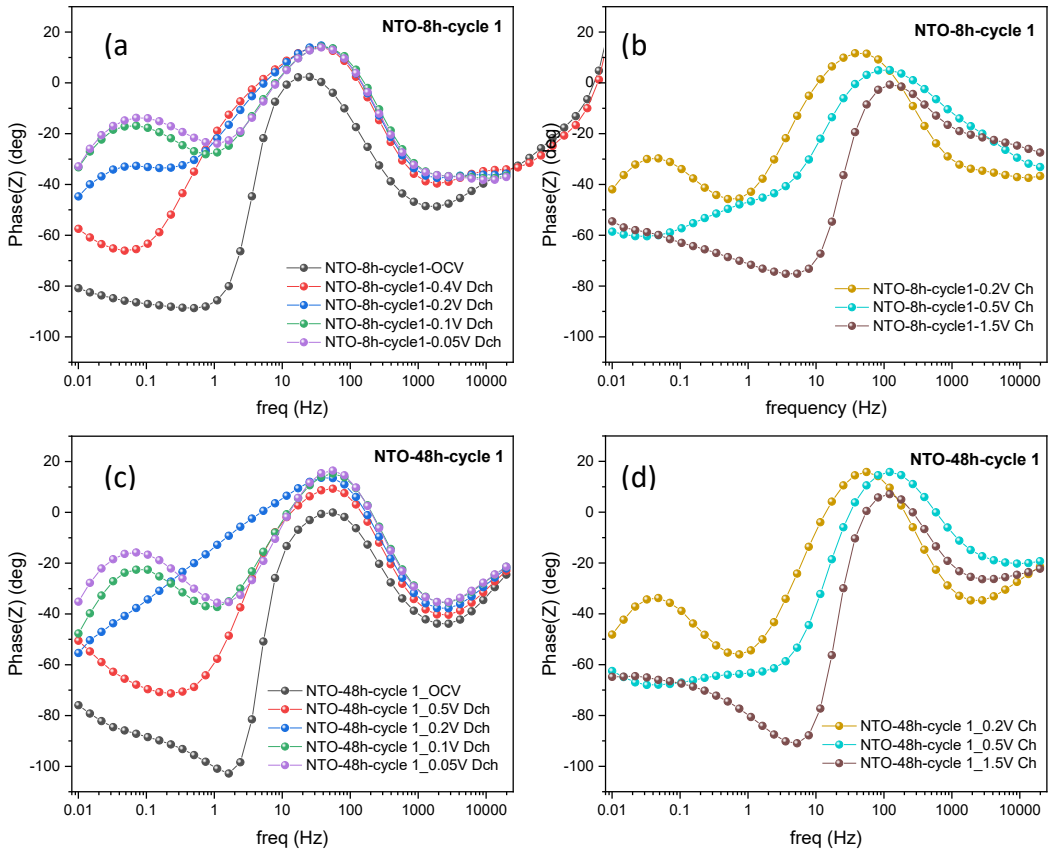


Figure S12. Bode plots of (a,b) NTO-8h and (c,d) NTO-48h showing the phase angle–frequency dependence at different voltage steps in the discharge and charge steps of the first cycle.

Table S4 : Impedance parameters derived using equivalent circuit models of NTO-8h-cycle 1

		NTO-8h-cycle 1-0.4V dch		NTO-8h-cycle 1-0.2V dch		NTO-8h-cycle 1-0.1V dch		NTO-8h-cycle 1-0.05V dch		NTO-8h-cycle 1-0.2V ch		NTO-8h-cycle 1-0.5V ch	
Element / Parameter	**Unit**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**
L	**H**	0.22289	0.07954	0.17103	0.03159	0.11577	0.07171	0.12515	0.0672	0.09528	0.06069	0.09993	0.00916
Q_{SEI}	**s^{α}/Ω**	4.05E-05	8.91E-05	2.62E-05	1.77E-05	3.39E-05	6.11E-05	2.89E-05	4.33E-05	2.31E-05	3.66E-05	0.00618	0.0011
α_{SEI}		0.68495	0.22199	0.71748	0.058	0.69586	0.17999	0.71697	0.15176	0.7323	0.15945	0.75413	0.06728
Q_{dl}	**s^{α}/Ω**	0.01588	0.00283	0.01565	3.49E-04	0.00613	9.33E-05	0.0056	9.65E-05	0.00463	2.71E-05	0.0057	0.00361
α_{dl}		0.92356	0.02247	0.83839	0.01449	0.87902	0.01163	0.84731	0.01215	0.88123	0.00593	0.78877	0.06119
Q_L	**s^{α}/Ω**	5.66E-06	7.30E-07	6.14E-06	8.53E-07	6.94E-06	1.10E-06	7.42E-06	1.18E-06	7.95E-06	1.50E-06	2.78E-05	9.16E-06
α_L		1	0.0378	1	0.0305	1	0.05428	1	0.05144	1	0.06052	0.69599	0.03918
Q_w	**s^{α}/Ω**	0.03841	0.01573	0.03653	0.00121	0.08399	0.0026	0.13419	0.00453	0.0289	5.68E-04	0.84408	87.4262
α_w		0.93381	0.08117	0.70762	0.00827	0.73746	0.00929	0.82377	0.01097	0.77895	0.00526	0.60429	4.09152
R_s	**Ω**	4.67619	2.59961	4.25	0	3.84252	2.15732	4.25	1.79343	4.17746	1.86369	3.64916	1.10001
R_{SEI}	**Ω**	19.7898	12.6925	20.7399	4.71081	24.2214	15.2578	24.5598	13.2928	23.3757	12.7068	52.8194	21.3516
R_{CT}	**Ω**	848.579	168.356	74.6321	3.42535	71.0775	1.47165	63.4911	1.20623	202.619	3.12191	7752.19	6694.59
$R_{L'}$	**Ω**	50.1811	9.74832	44.3964	4.98326	36.9972	12.3726	37.8714	11.2897	30.738	10.7631	26.0022	1.62649
$R_{L''}$	**Ω**	20.0434	18.4946	11.5414	7.08918	4.92532	16.5152	5.29256	14.7317	2.78668	12.946	26.9752	4.12915
χ^2		**0.01453**		**0.02404**		**0.02045**		**0.01546**		**0.02941**		**0.01787**	

Table S5 : Impedance parameters derived using equivalent circuit models of NTO-8h-cycle 2

		NTO-8h-cycle 2-0.5V dch		NTO-8h-cycle 2-0.2V dch		NTO-8h-cycle 2-0.15V dch		NTO-8h-cycle 2-0.05V dch		NTO-8h-cycle 2-0.35V ch		NTO-8h-cycle 2-0.5V ch		NTO-8h-cycle 2-1.5V ch	
Element / Parameter	**Unit**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**
L	**H**	0.10169	0.05781	0.08988	0.072	0.0964	0.06876	0.07555	0.05472	0.01364	0.02191	0.03206	0.00817	0.0525	1.74E-09
Q_{SEI}	**s^q/Ω**	1.37E-04	3.75E-04	1.03E-04	4.34E-04	8.46E-05	3.38E-04	6.14E-05	2.58E-04	1.17E-06	1.44E-05	0.00355	1.11E-04	9.66E-04	0.00698
α_{SEI}		0.55732	0.28083	0.59979	0.41893	0.62174	0.39923	0.64977	0.41958	0.9659	1.30506	0.76935	0.02306	0.88014	0.10966
Q_{dl}	**s^q/Ω**	0.00526	1.62E-05	0.00689	0.0029	0.00585	0.00186	0.00505	7.37E-04	0.00799	0.0072	0.00487	1.38E-04	9.69E-04	0.00697
α_{dl}		0.728	0.00642	0.80068	0.09896	0.77827	0.0959	0.85531	0.08571	0.72152	0.15563	0.91085	0.00955	0.97287	0.10679
Q_L	**s^q/Ω**	1.36E-05	2.74E-06	9.14E-06	1.82E-06	8.84E-06	1.70E-06	8.20E-06	1.69E-06	5.23E-06	2.99E-06	9.60E-06	6.01E-06	2.75E-05	0.0071
α_L		1	0.05747	1	0.06728	1	0.06262	1	0.06489	0.98874	0.14266	0.79049	0.0797	0.69285	0.07909
Q_w	**s^q/Ω**	0.02841	0.00973	0.03827	0.04578	0.04418	0.06129	0.09058	0.1054	0.01324	0.01656	1897.49	0.02482	0.0015	0.00696
α_w		0.96381	0.07217	0.72372	0.58343	0.58961	0.44787	0.51494	0.46488	0.67786	0.2418	0.1	998.787	0.96037	0.1201
R_s	**Ω**	3.26341	4.35522	4.27575	4.69942	4.60264	4.27498	4.68567	4.26176	4.97512	10.3221	4.5468	0	4.92549	0.58604
R_{SEI}	**Ω**	18.8977	13.6712	16.3511	18.7865	15.8627	17.0319	14.6566	15.8283	6.60894	17.9673	85.9209	9.10264	192.376	19.0115
R_{CT}	**Ω**	11047.5	4011.19	72.7803	56.827	90.4327	53.7692	38.6455	15.2741	213.432	350.578	1048.28	0	1186.09	138.195
$R_{L'}$	**Ω**	25.3132	7.64718	28.0812	11.612	29.4972	10.9918	27.3855	10.5031	10.0102	8.5455	13.7408	2.22485	16.5434	2.35821
$R_{L''}$	**Ω**	4.30945	11.8925	5.44542	18.4462	4.65503	16.2419	4.66022	15.4558	0.009	8.40257	9.62488	4.57772	45.1806	5.63184
χ^2		**0.01136**		**0.01323**		**0.00983**		**0.01191**		**0.03111**		**0.03787**		**0.01052**	

Table S6 : Impedance parameters derived using equivalent circuit models of NTO-48h-cycle 1.

		NTO-48h-cycle 1-0.4V dch		NTO-48h-cycle 1-0.2V dch		NTO-48h-cycle 1-0.1V dch		NTO-48h-cycle 1-0.05V dch		NTO-48h-cycle 1-0.2V ch		NTO-48h-cycle 1-0.5V ch	
Element /Parameter	Unit	Value	±	Value	±	Value	±	Value	±	Value	±	Value	±
L	H	0.105886	0.112761	0.052911	0.156604	0.052548	0.0596134	0.055554	0.0462713	0.046242	0.0767161	0.013578	0.00168147
Q_{SEI}	s^{α}/Ω	3.14E-05	6.86033E-05	4.66E-05	7.53227E-05	3.83E-05	0.000142833	3.18E-05	0.000113552	5.14E-05	0.000177745	0.012911	0.00300472
α_{SEI}		0.826029	0.249466	0.788168	0.204635	0.802942	0.392015	0.819564	0.373237	0.770506	0.365693	0.887143	0.0881315
Q_{dl}	s^{α}/Ω	0.004758	0.00171575	0.114445	0.0226323	0.007229	9.07702E-05	0.00593	7.86021E-05	0.005222	3.41343E-05	0.005685	0.00429721
α_{dl}		0.903932	0.0319486	0.781703	0.0947181	0.867776	0.0104095	0.84907	0.0094033	0.90784	0.00576464	0.836496	0.0684202
Q_L	s^{α}/Ω	9.09E-06	2.33139E-06	1.24E-05	7.87243E-06	9.83E-06	2.80861E-06	9.79E-06	2.55391E-06	1.09E-05	3.62707E-06	2.68E-05	1.59781E-05
α_L		1	0.0897357	1	0.149398	1	0.0921509	1	0.0781595	1	0.108418	0.811833	0.0692771
Q_w	s^{α}/Ω	0.017091	0.0200694	0.064613	0.00517128	0.093849	0.00218006	0.184071	0.00527323	0.027948	0.00062732	0.079622	0.879776
α_w		0.990813	0.284732	0.733991	0.0179918	0.851182	0.00689533	0.883588	0.00934239	0.804144	0.00656933	0.793309	0.957595
R_s	Ω	5.60845	0.946875	5.66161	0.939918	5.60601	1.3148	5.68916	1.25694	5.70372	1.36985	6.23521	0.666585
R_{SEI}	Ω	10.5131	17.1185	13.6953	34.0161	7.91952	14.2355	7.4287	10.9374	9.58225	19.5687	29.9245	13.3805
R_{CT}	Ω	1664.08	746.921	14.7978	5.92156	69.0698	1.19671	66.7178	0.87687	193.577	3.17817	7609.2	7992.67
$R_{L'}$	Ω	28.0239	16.8054	20.136	31.8203	21.0352	13.2387	21.7708	10.2441	19.8088	17.7302	10.7844	1.05227
$R_{L''}$	Ω	12.5171	30.7979	1.05082	36.4421	2.98872	16.778	2.17598	11.8546	0.013944	18.281	0.382068	0.87791
χ^2		**0.073795**		**0.019623**		**0.022505**		**0.020577**		**0.027184**		**0.082129**	

Table S7 : Impedance parameters derived using equivalent circuit models of NTO-48h-cycle 2.

		NTO-48h-cycle 2-0.5V dch		NTO-48h-cycle 2-0.25V dch		NTO-48h-cycle 2-0.17V dch		NTO-48h-cycle 2-0.05V dch		NTO-48h-cycle 2-0.35V ch		NTO-48h-cycle 2-0.5V ch	
Element /Parameter	**Unit**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**	**Value**	**±**
L	**H**	0.031695	0.00782345	0.024649	0.0349002	0.021651	0.00503572	0.018041	0.00438997	0.011651	1.53446E-09	0.005586	0.00177911
Q_{SEI}	**s^{α}/Ω**	0.002681	0.00226144	5.62E-06	0.000453739	0.003269	0.00729997	0.002701	0.00746969	0.00629	0.00251736	0.00476	0.114946
α_{SEI}		1	0.61917	1	7.14183	1	0.847116	1	0.552226	0.967458	0.43547	1	5.8291
Q_{dl}	**s^{α}/Ω**	0.004773	0.104924	0.003781	0.00370485	0.007879	0.0333336	0.007971	0.0603271	0.004456	0.00344418	0.002415	0.010269
α_{dl}		0.873145	2.13777	0.911494	0.309147	0.922828	1.55379	0.984284	1.46187	1	0.450271	1	1.10843
Q_L	**s^{α}/Ω**	2.04E-05	2.67582E-05	2.06E-05	6.36974E-05	2.94E-05	4.84048E-05	4.46E-05	7.67768E-05	0.000247	0.00525624	8.08E-05	0.000162011
α_L		0.82976	0.148796	0.838811	0.491902	0.791905	0.181965	0.749556	0.191894	0.50209	0.221742	0.650327	0.201827
Q_w	**s^{α}/Ω**	0.015804	1.05586	0.029478	0.00628371	0.03196	0.0751565	0.095761	0.196015	0.035901	0.0101348	0.011121	0.481777
α_w		0.939802	0.01911	0.761626	0.101868	0.718714	0.654694	0.772188	0.633305	0.921455	0.45084	1	12.2122
R_s	**Ω**	8.46695	2.40356	7.95773	0	8.30361	2.54399	8.08578	2.59985	4.23467	225.806	5.46881	1.6489
R_{SEI}	**Ω**	73.8512	193.907	1.08605	17.3232	27.8018	189.097	37.2114	251.554	508.216	25.7211	464.893	18515.7
R_{CT}	**Ω**	2149.68	57482.7	16.262	9.26551	91.0257	370.176	53.2113	298.156	55.7638	9.34016	90.5206	871.21
$R_{L'}$	**Ω**	23.4028	5.12004	22.2896	25.7944	22.2968	5.60352	21.2632	5.69904	20.6499	0	13.6628	3.69507
$R_{L''}$	**Ω**	2.41528	6.96186	2.656	22.1715	2.10028	4.03093	1.18522	3.55288	2.28398	0	1.10005	0
χ^2		**0.086139**		**0.03892**		**0.044655**		**0.034496**		**0.201147**		**0.460405**	