Supporting Information

Composition and Evolution of the Solid-Electrolyte Interphase in $Na_2Ti_3O_7$ Electrodes for Na-ion Batteries: XPS and Auger Parameter Analysis

Miguel A. Muñoz-Márquez,[*,†] *Maider Zarrabeitia,*[†] *Elizabeth Castillo-Martínez,*[†] *Aitor Eguía-Barrio,*[‡] *Teófilo Rojo,*[†,‡] *Montse Casas-Cabanas*[†]

[†] CIC Energigune, Parque Tecnológico de Álava, Albert Einstein 48, 01510 – Miñano, Spain.

[‡] Departamento de Química Inorgánica, Universidad del País Vasco UPV/EHU, P.O. Box 644, 48080 - Bilbao, Spain.

* Corresponding author: mamunoz@cicenergigune.com

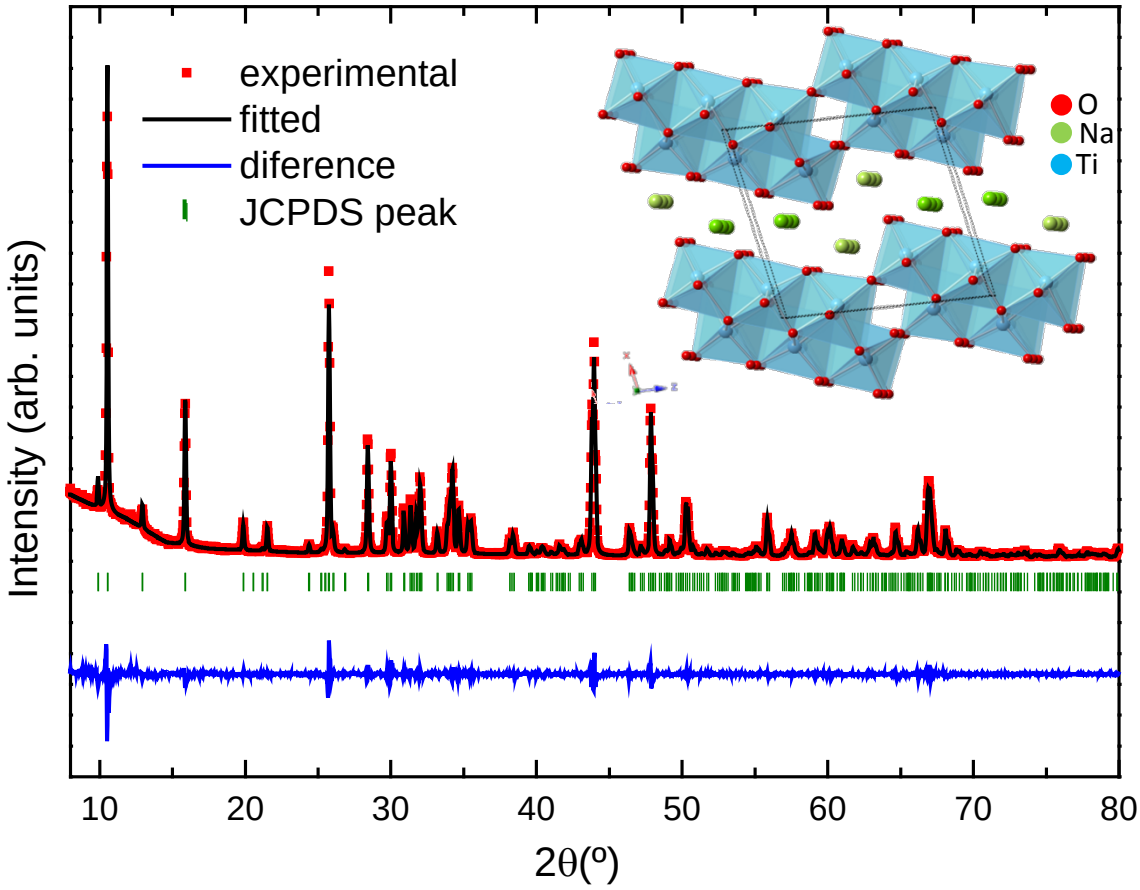

Figure S1. Rietveld refined XRD pattern of $Na_2Ti_3O_7$ with inset showing the crystal structure.

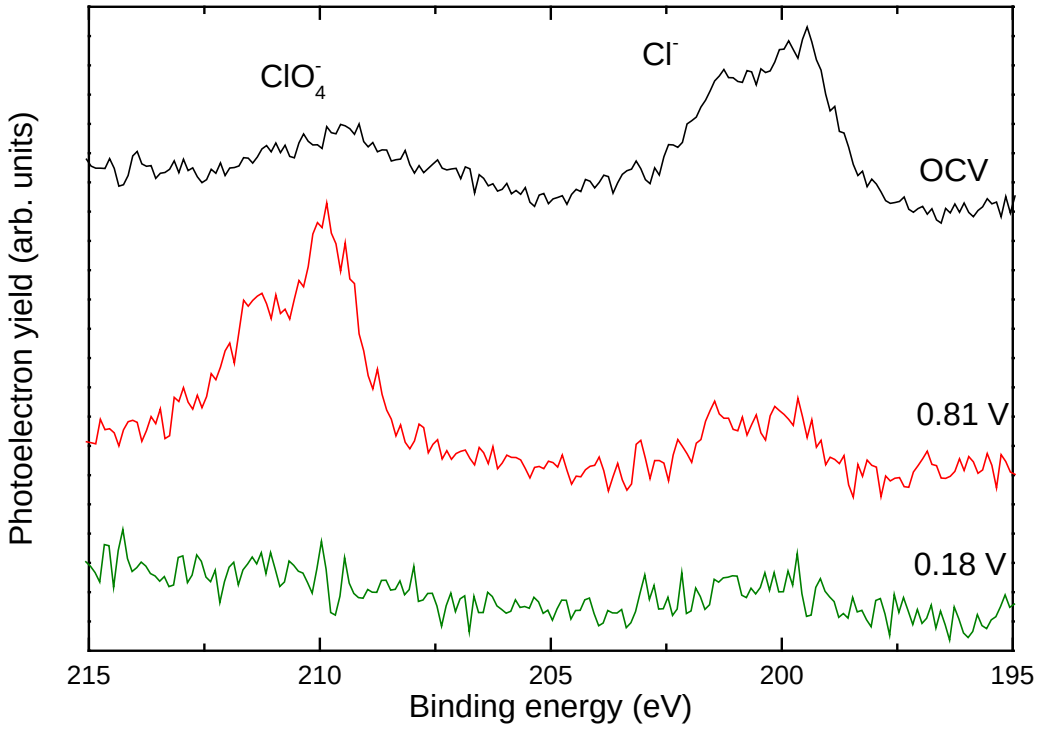

Figure S2. XPS spectrum of the Cl 2*p* photoelectron line for the electrode at OCV and before and after the SEI formation, 0.8 V and 0.2 V respectively. This shows how NaCl is formed at the very beginning of the electrochemical cycling just after cell assembly. Traces of $NaClO_4$ not removed during washing are detected.

Table S1. Results of the Rietveld refinement.

Parameter	Value
a	8.5647(2) Å
b	3.79817(7) Å
c	9.1226(2) Å
β	101.604(2) deg
$\mathbf{R_p}$	14.6 %
χ^2	4.042

Table S2. Experimental photoemission lines and Auger parameters measured from reference compounds. For insulating compounds charging was compensated using an electron flood gun working at 1.5 V with a emission current of 10 μA.

Sample	Na 1*s*	F 1*s*	O 1*s*	C 1*s*	Na $KL_{23}L_{23}$ (eV)	Cl 2*p*	α + hν	ΔE_{O-C}	ΔE_{F-C}	ΔE_{O-Cl}
Na_2CO_3	1070.98		530.83	289.40	990.46		2061.4	241.43		
PVdF		689.10	533.30	291.95				241.35	397.15	
$NaClO_4$	1070.22		532.49[a] 530.77[b]		989.22	208.26[a] 206.02[b] 197.98[c]	2060.1			324.23[a] 324.75[b]
C65				284.37						
$Na_2Ti_3O_7$	1072.53				989.40		2061.9			

[a] Data corresponding to the ClO_4^- group.

[b] Data corresponding to the ClO_3^- group. As discussed in the manuscript it is related to the photoinduced decomposition of the perchlorate.

[c] Data corresponding to the Cl^- anion.

Table S3. Experimental Auger parameters of the Na-based compounds of the SEI layer at different charge states along with their assignation.

Charge state	Na $KL_{23}L_{23}$ peak position Kinetic energy [a] (eV)	Na 1s peak position Binding energy [a] (eV)	α + hν $E_K + E_B$ [b]
Pristine	989.28	1072.72	2062.0
OCV	989.07	1072.69	2061.8
0.81 V	988.51	1072.77	2061.3
0.18 V	988.29	1072.83	2061.1
1st disch.	988.20	1072.88	2061.1
1st ch.	988.36	1072.90	2061.3
2nd disch.	988.29	1072.78	2061.1
3rd ch.	988.48	1072.72	2061.2

[a] Error for E_K and E_B is ±0.05 eV
[b] Error Auger parameter is ±0.1 eV