

Supplementary Information

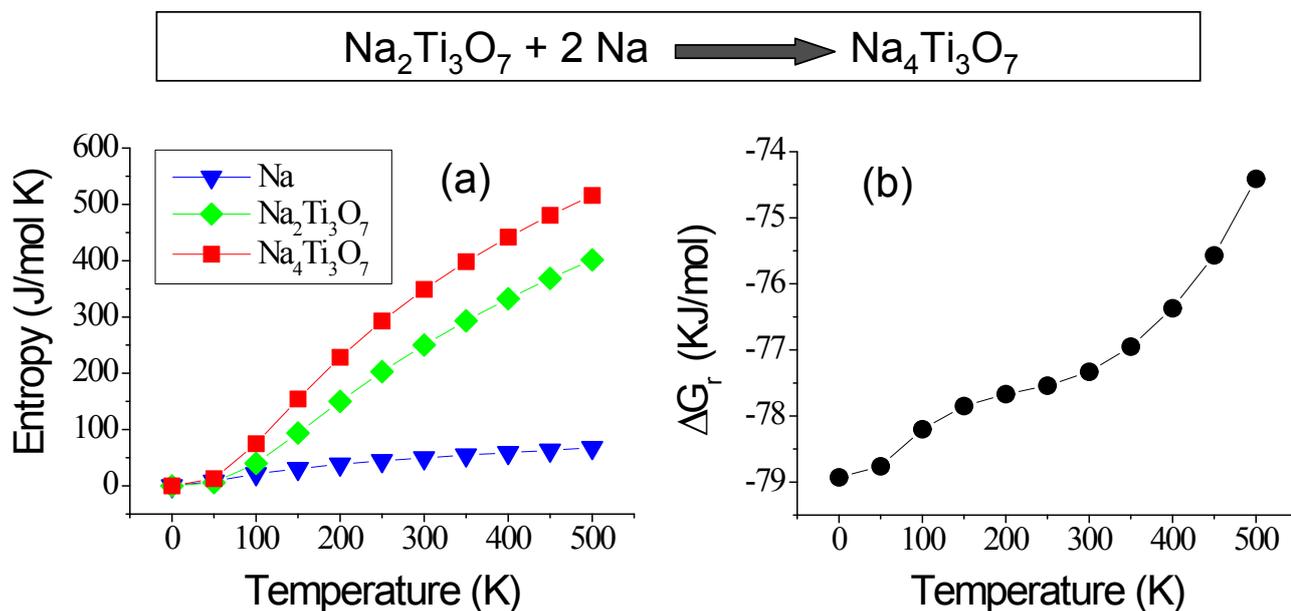


Figure S1.- Left: Estimated entropy of Na (blue triangles), Na₂Ti₃O₇ (green diamonds) and Na₄Ti₃O₇ (red squares). Right: Evolution of the free energy (ΔG) of the Na insertion reaction in Na₂Ti₃O₇ with temperature.

Conditions for the mechanical stability of a monoclinic crystal

$$\begin{aligned}
 &C_{11} > 0, \quad C_{22} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{55} > 0, \quad C_{66} > 0, \\
 &(C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) > 0, \\
 &(C_{33}C_{66} - C_{36}^2) > 0, \quad (C_{44}C_{55} - C_{45}^2) > 0, \\
 &(C_{22} + C_{33} - 2C_{23}) > 0, \\
 &[C_{22}(C_{33}C_{66} - C_{36}^2) + 2C_{23}C_{26}C_{36} - C_{23}^2C_{66} - C_{26}^2C_{33}] > 0, \\
 &\{2[C_{16}C_{26}(C_{33}C_{12} - C_{13}C_{23}) + C_{16}C_{36}(C_{22}C_{13} - C_{12}C_{23}) + \\
 &+ C_{26}C_{36}(C_{11}C_{23} - C_{12}C_{13})] - [C_{16}^2(C_{22}C_{33} - C_{23}^2) + \\
 &+ C_{26}^2(C_{11}C_{33} - C_{13}^2) + C_{36}^2(C_{11}C_{22} - C_{12}^2)] + \\
 &+ C_{66}^2(C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23})\} > 0
 \end{aligned}$$

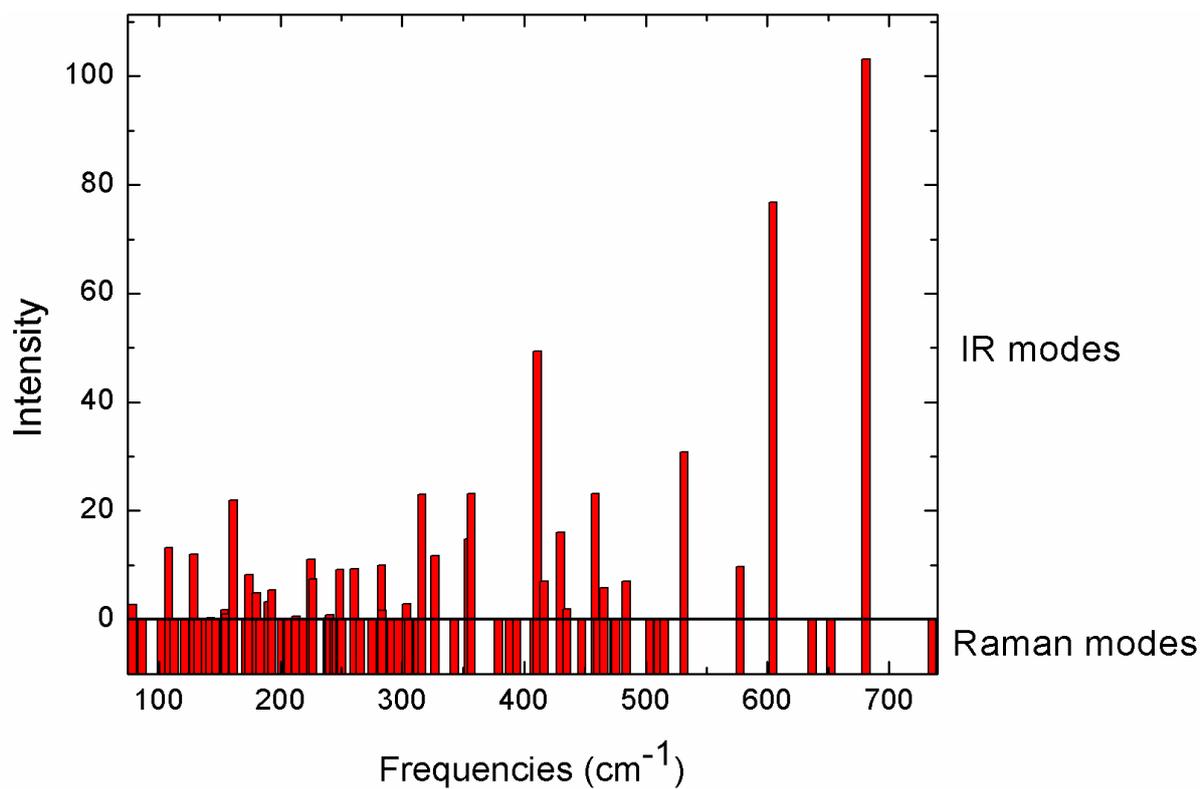


Figure S2. Vibrational modes of $\text{Na}_4\text{Ti}_3\text{O}_7$ in the γ -point. The modes with intensity value up to 0 correspond to Raman modes and the modes with intensities greater than zero are active in IR.

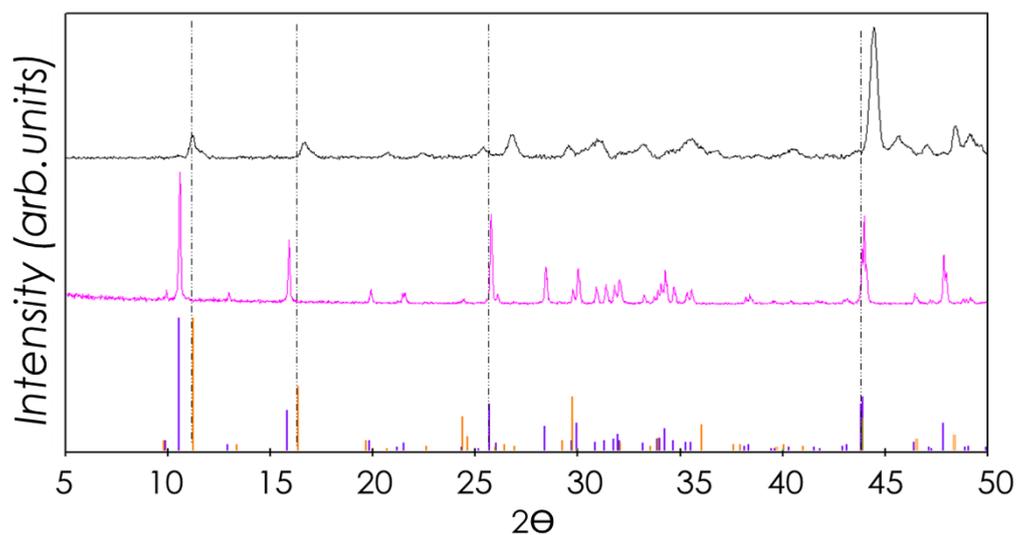


Figure S3. XRPD pattern of pristine $\text{Na}_2\text{Ti}_3\text{O}_7$ (pink) and a self-standing electrode fabricated with $\text{Na}_2\text{Ti}_3\text{O}_7$ (black). Peak positions and intensities for $\text{Na}_2\text{Ti}_3\text{O}_7$ (purple, PDF#31-1329) and $\text{H}_2\text{Ti}_3\text{O}_7$ (orange PDF#47-561)) are shown in the lower part of the graph.

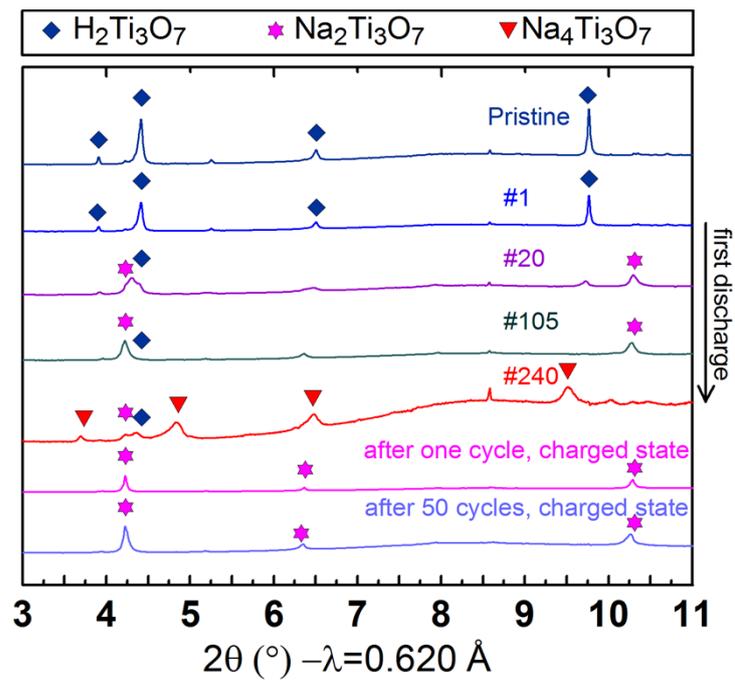


Figure S4. Selected SXRD patterns along the first discharge of the cell together with one collected after 50 cycles in the charged state.