Supplementary Information (SI) for EES Batteries.

Ti-induced Surface Stabilization for Enhanced Capacity of Aqueous-Processed Ni-Rich Cathodes

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Supplementary Figures

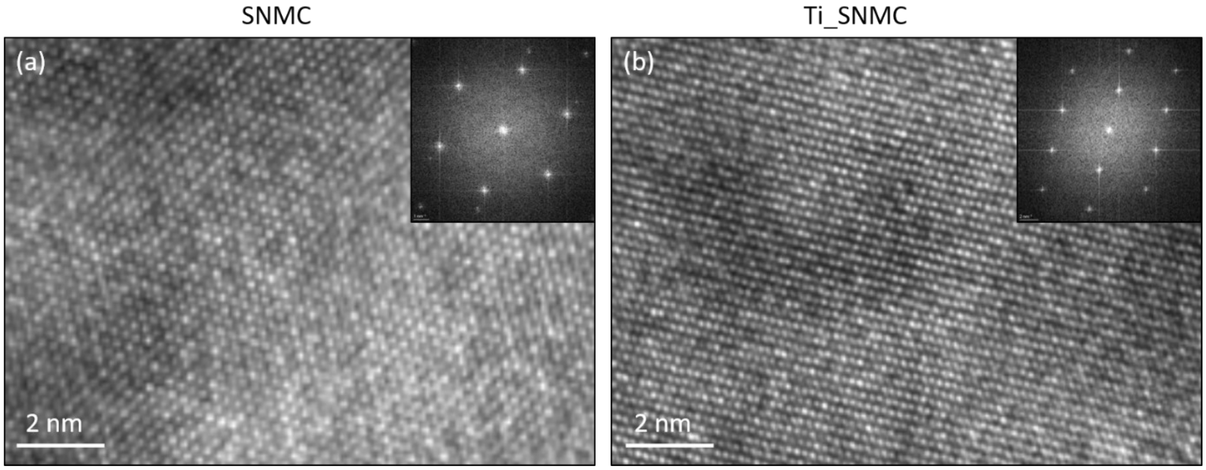

Figure S1. High-resolution TEM images and corresponding Fourier transform (FT) patterns (inset) of sample Pristine SNMC (a) and Ti-SNMC (b) electrodes. The images and the FT patterns show the particles are single-crystalline. The FT patterns of the two samples are different due to the different alignment of the zone axes of the two lamellae with respect to the electron beam axis.

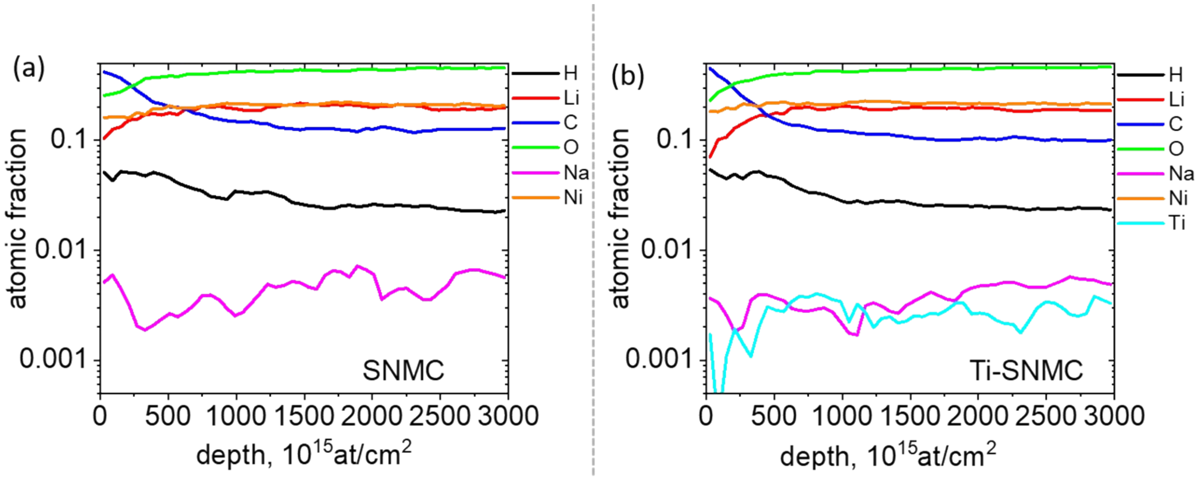

Figure S2. Depth profiling of the element composition of SNMC (a), and Ti-SNMC (b) electrodes.

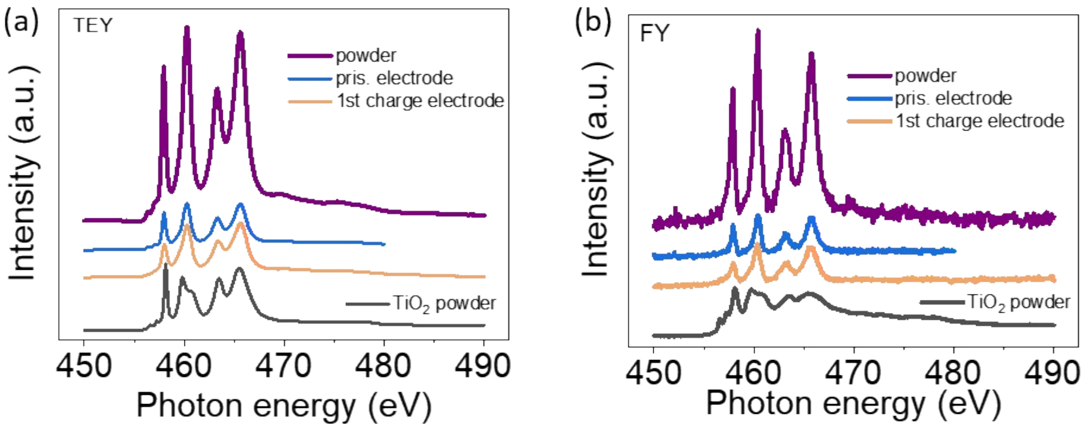

Figure S3. Ti $L_{2,3}$-edge XAS-TEY (a) and XAS-FY (b) spectra of Ti-SNMC powder, pristine, 1st charge Ti-SNMC electrode and TiO_2 powder.

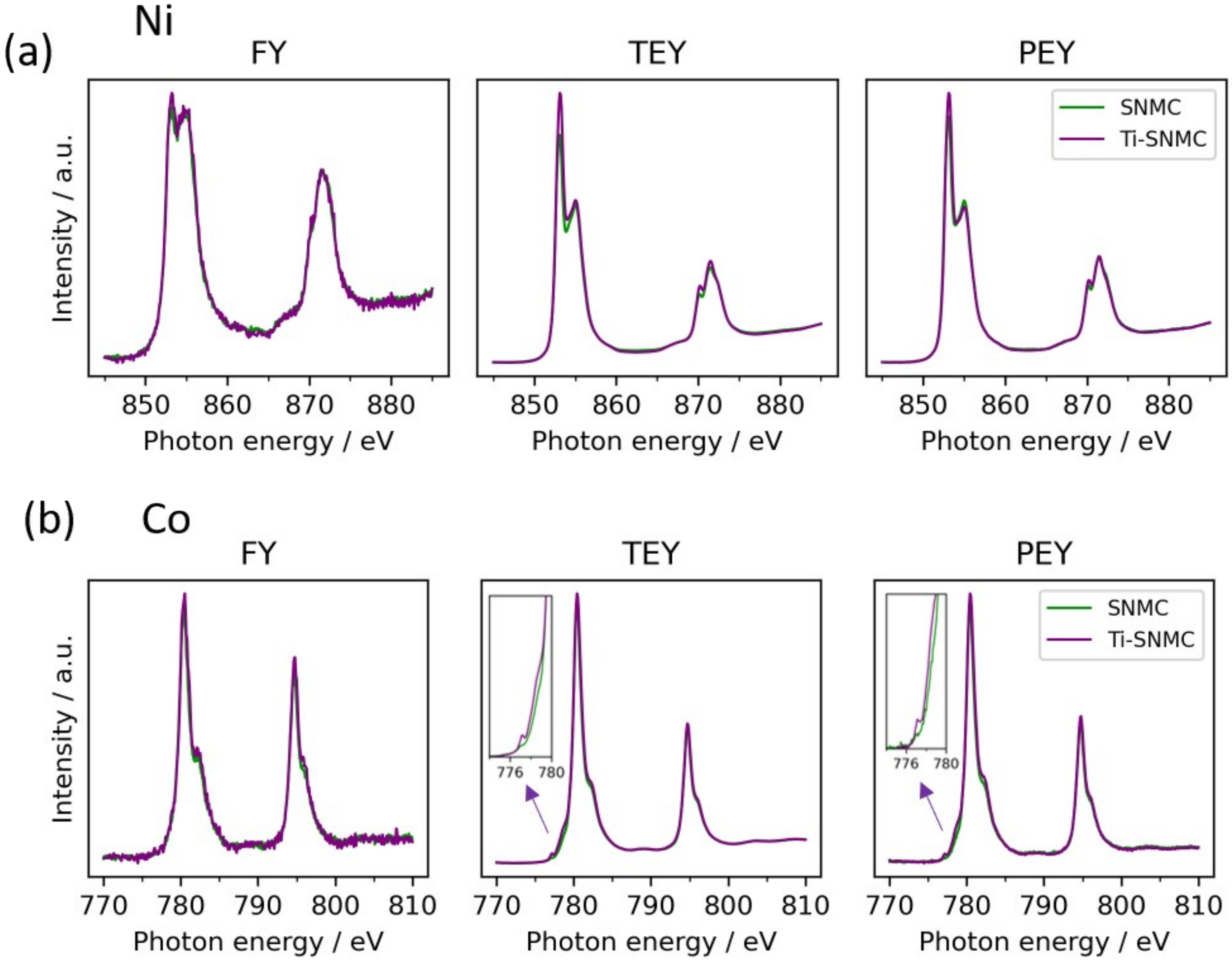

Figure S4. XAS-FY, XAS-TEY, and XAS-PEY spectra of Ni $L_{2,3}$-edge (a) and Co $L_{2,3}$-edge (b), collected from SNMC and Ti-SNMC powder.

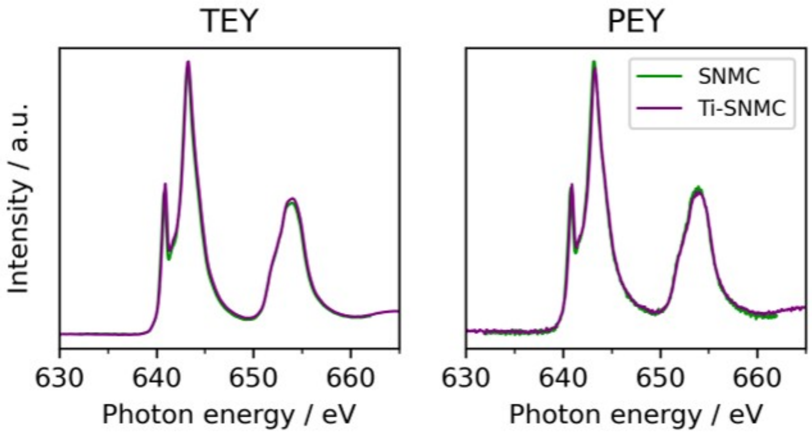

Figure S5. XAS-TEY, and XAS-PEY spectra of Mn $L_{2,3}$-edge collected from SNMC and Ti-SNMC powder.

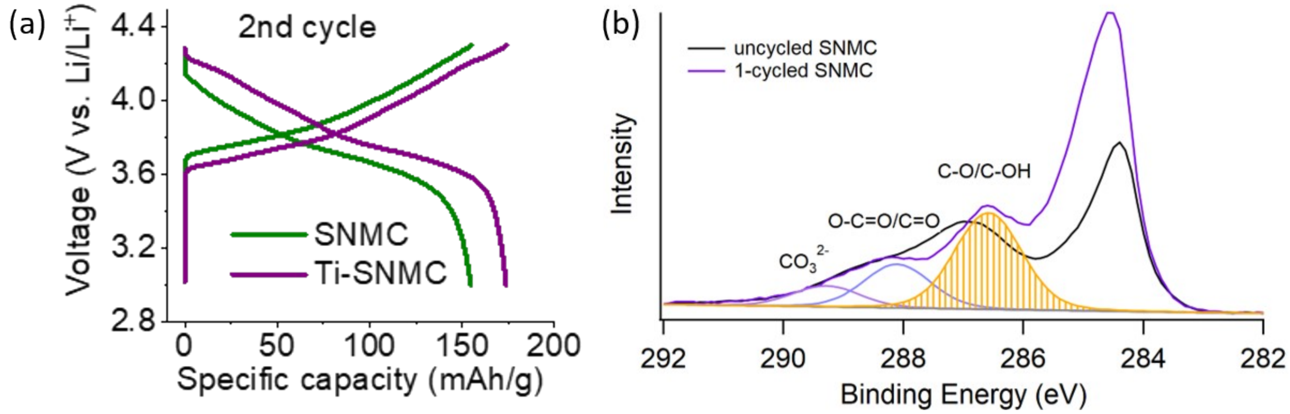

Figure S6. (a) Charge-discharge capacity profile of 2nd cycle of SNMC and Ti-SNMC electrodes. (b) C 1s spectra of the SNMC electrode as uncycled and after the initial cycle. Spectra are normalized to the background intensity at 282 eV.

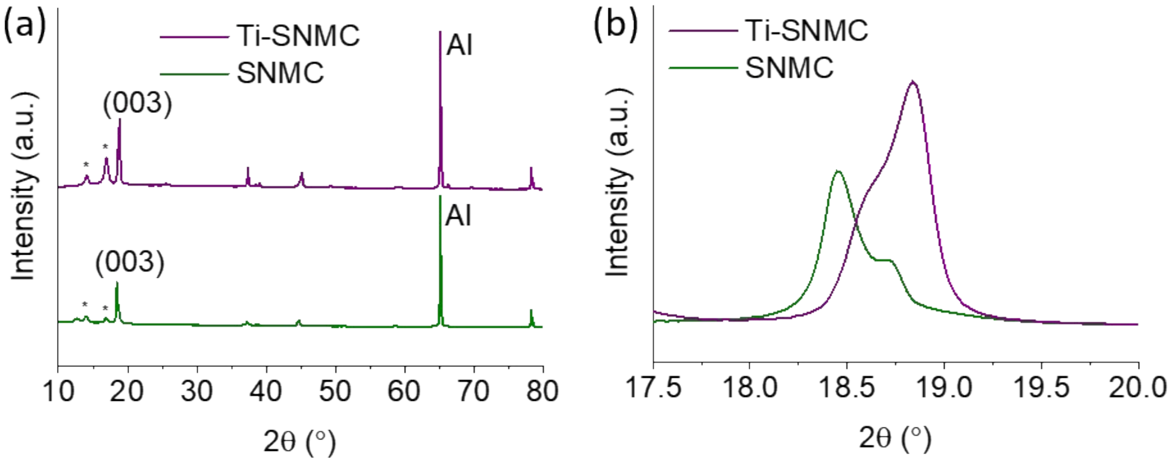

Figure S7. (a) XRD patterns showing (b) (003) reflection for the SNMC and Ti-SNMC electrodes measured at the charged state (4.3 V vs. Li^+/Li). Both XRD patterns are calibrated with the reflection peak of Al from the current collector.

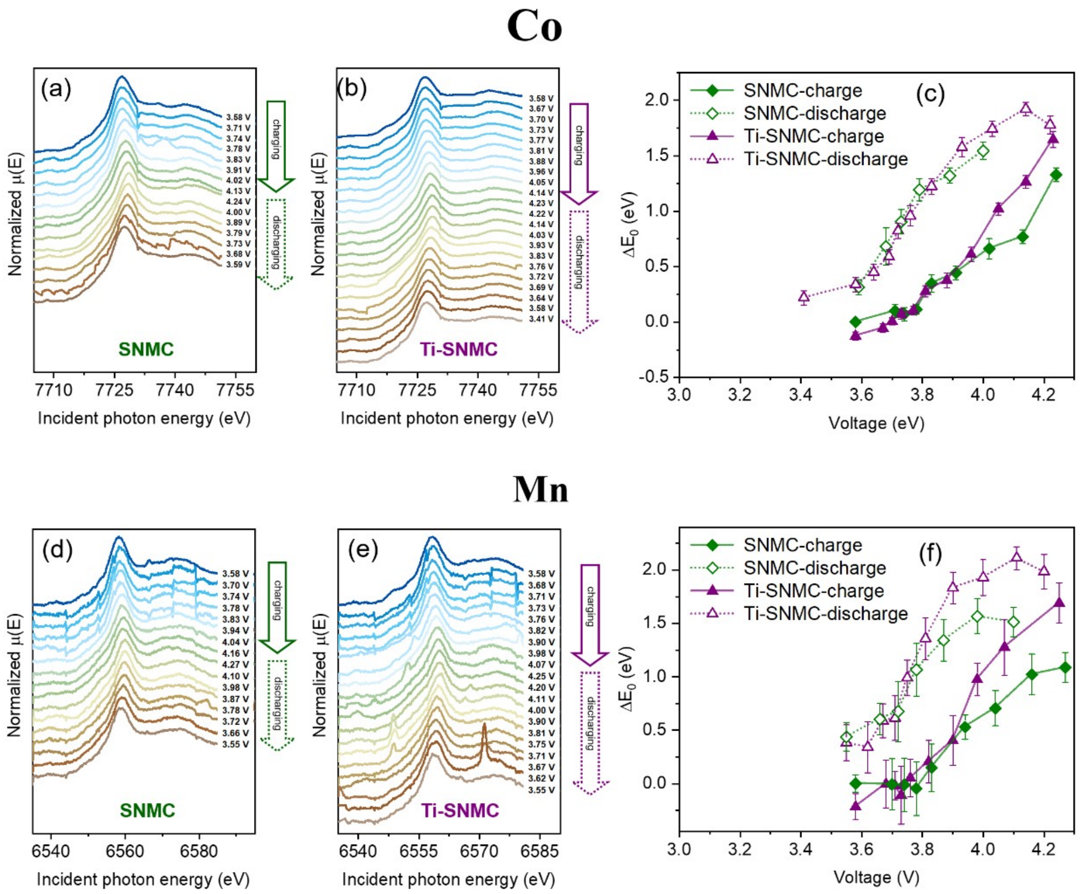

Figure S8. Normalized *K*-edge XANES spectra of Co (top panel) and Mn (bottom panel) collected operando from (a, d) SNMC and (b, e) Ti-SNMC electrodes at different voltages during charging-discharging. Comparative evolution of chemical shifts for Co (c) and Mn (f) ions for SNMC (green diamonds) and Ti-SNMC (purple triangles) cathodes under different operating voltages during charging (closed circles) and discharging (open symbols).

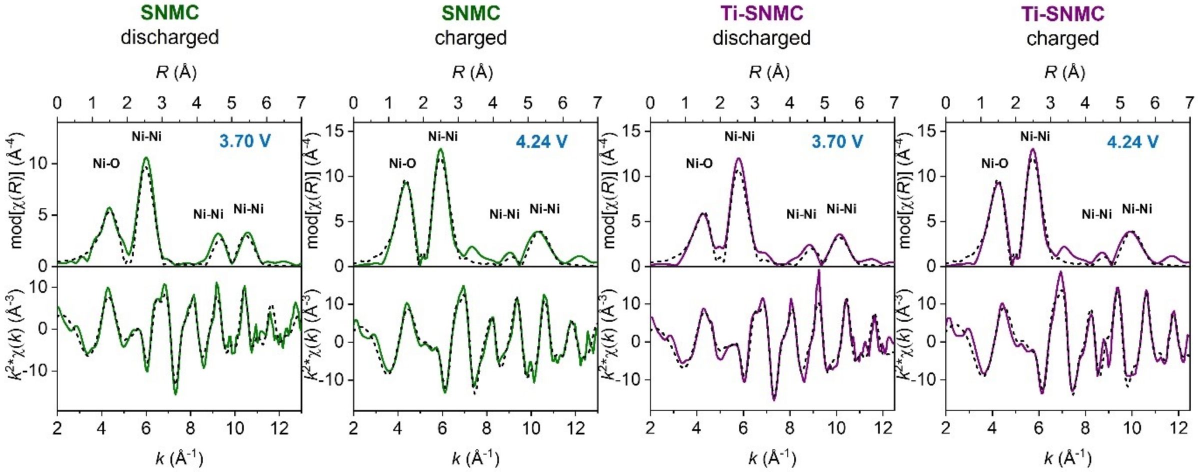

Figure S9. k^3-weighted Ni *K*-edge EXAFS (lower panel) and corresponding modulus of Fourier transformed EXAFS (upper panel) for the SNMC cathodes (green) in the fully discharged (3.70 V), and fully charged (4.24 V) states; corresponding spectra of the Ti-SNMC cathodes (magenta) in the fully discharged (3.70 V), and fully charged (4.24 V) states. The fits (feff modeled spectra) are shown in black dotted curves.

Supplementary Table

Table S1. Concentration of transition metals in SNMC and Ti-SNMC particles from Inductively coupled plasma atomic emission spectrometry (ICP-OES) measurements.

Materials	Ni/ %	Co/ %	Mn/ %	Ti/ %
SNMC	79.9	10.1	10.0	-
Ti-SNMC	79.7	10.0	9.8	0.5

Table S2. PES peak fitting parameters for C 1s, O 1s, F 1s, and P 2p spectra.

C 1s	Peak assignment	Binding energy (eV)	O 1s	Peak assignment	Binding energy (eV)
	C=C	~284.5		M-O	~529.2
	C-H	285		Surface O	~531
	C-O/C-OH	~286.7		C=O	~532.1
	C=O/ O=C-O	~288.2		C-O/P=O	~533.3
	CO_3^{2-}	~289.4		C-OH	~534.2
F 1s	LiF	~684.7	P 2p	PO_4^{3-}	~133.2
	$Li_xPO_yF_z$	~686		$Li_xPO_yF_z$	~134.6
	$LiPF_6$	~687.5		$LiPF_6$	~135.5

Table S3. Ni *K*-edge EXAFS simulation parameters of the k^3-weighted EXAFS spectra of SNMC and Ti-SNMC materials in the discharged (3.70 V) and charged (4.24 V) states. A multiple scattering path was included in the fit but not shown in the table.

	Path	**R (Å)**	**σ^2 (Å^2)**	**CN**	**R_f [b]**	**BVS [c]**
SNMC **3.70 V**	Ni-O	1.94 ± 0.01	0.013 ± 0.001	6*	24.7	3.1
	Ni-Ni	2.86 ± 0.01	0.006 ± 0.001	6*		
	Ni-Ni	5.00 ± 0.01	0.006 ± 0.001	6*		
	Ni-Ni [a]	5.72*	0.008 ± 0.001	6*		
SNMC **4.24 V**	Ni-O	1.87 ± 0.01	0.007 ± 0.001	6*	20.3	4.0
	Ni-Ni	2.82 ± 0.01	0.005 ± 0.001	6*		
	Ni-Ni	4.89 ± 0.01	0.008 ± 0.002	6*		
	Ni-Ni [a]	5.63*	0.008 ± 0.001	6*		
Ti-SNMC **3.70 V**	Ni-O	1.93 ± 0.01	0.012 ± 0.001	6*	21.4	3.2
	Ni-Ni	2.86 ± 0.01	0.005 ± 0.001	6*		
	Ni-Ni	4.99 ± 0.01	0.007 ± 0.001	6*		
	Ni-Ni [a]	5.72*	0.007 ± 0.001	6*		
Ti-SNMC **4.24 V**	Ni-O	1.87 ± 0.01	0.007 ± 0.001	6*	25.0	4.0
	Ni-Ni	2.82 ± 0.01	0.005 ± 0.001	6*		
	Ni-Ni	4.88 ± 0.04	0.015 ± 0.005	6*		
	Ni-Ni [a]	5.64*	0.006 ± 0.001	6*		

* Parameters marked with an asterisk were fixed during the optimization procedure

[a] This is double distance of the 1st Ni-Ni shell (2 * $R_{Ni\text{-}Ni}$) and was not minimized in the simulation

[b] The R_f value is an estimate of the quality of the fit, and represents the percentage error between the simulated spectra (fit) and the spectra

[c] The BVS represents the bond valence sum, and is an estimate of the oxidation state