

Supporting Information

Synergistic Effect of Co and Mn co-doping on SnO₂ Lithium-Ion Anodes

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Table S1. Starting structural model for SnO₂ that was used for the Rietveld refinement of the XRD data recorded for SCMO and SCMO@C: Graphical representation of the structure and main structural information (Occ = occupancy).

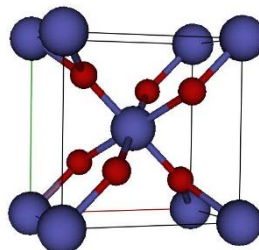
Space group $P4_2/mnm$ (136)

Cell length a = Cell length b = 4.832336 Å

Cell length c = 3.243221 Å

Cell angle α = β = γ = 90°

Z = 2



Atom	X	Y	Z	Occ	Multiplicity
Sn	0.0	0.0	0.0	1.0	2
O	0.193448	0.806552 (= 1-X)	0.5	1.0	4

Table S2. Results of the Rietveld refinement and the applied constraints. The values given in brackets indicate the error.

Sample	SCMO	SCMO@C
R_{wp} / %	5.80696	7.55588
a / Å	4.7484(2)	4.7498(3)
c / Å	3.1785(2)	3.1802(2)
Vol / Å³	71.667(7)	71.748(7)
Domain size (equatorial) / μm	0.00606(4)	0.00633(4)
Domain size (axial) / μm	0.01040(6)	0.01126(8)
U_{iso}(Sn)	0.0143(4)	0.0094(4)
Occ(Sn)	0.950(5)	0.952(4)
Occ(Mn)	0.025(2)	0.024(2)
X(O)	0.1991(7)	0.1989(8)

1. $U_{iso}(Sn) = U_{iso}(Mn) = U_{iso}(Co)$
2. $Occ(Sn) + Occ(Mn) + Occ(Co) = 1$
3. $Occ(Mn) = Occ(Co)$
4. $X(Sn) = X(Mn) = X(Co) = 0, \quad Y(Sn) = Y(Mn) = Y(Co) = 0, \quad Z(Sn) = Z(Mn) = Z(Co) = 0$

Table S3. Comparison of the experimental Mn and Co K-edge absorbance edge step with values that were calculated for a composition of $\text{Sn}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ and $\text{Sn}_{0.95}\text{Co}_{0.025}\text{Mn}_{0.025}\text{O}_2$, following the results of the Rietveld refinement of the XRD data, the EDX data, and the initial precursor ratio. The experimental values were recorded in transmission mode.

K-edge absorbance step	Experimental	Calculated	
		$\text{Sn}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$	$\text{Sn}_{0.95}\text{Co}_{0.025}\text{Mn}_{0.025}\text{O}_2$
Mn	0.014	0.024	0.011
Co	0.017	0.029	0.014

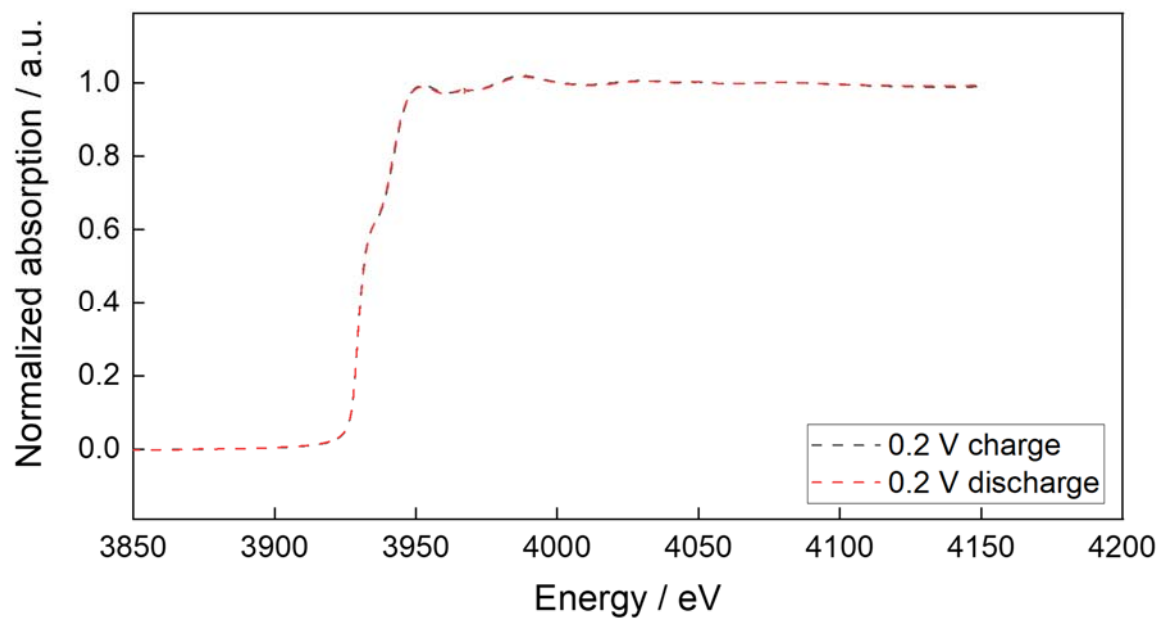


Figure S1. Comparison of the Sn L₃-edge X-ray absorption spectra of the SCMO@C-based electrodes discharged (in red) and charged (in black) to 0.2 V.

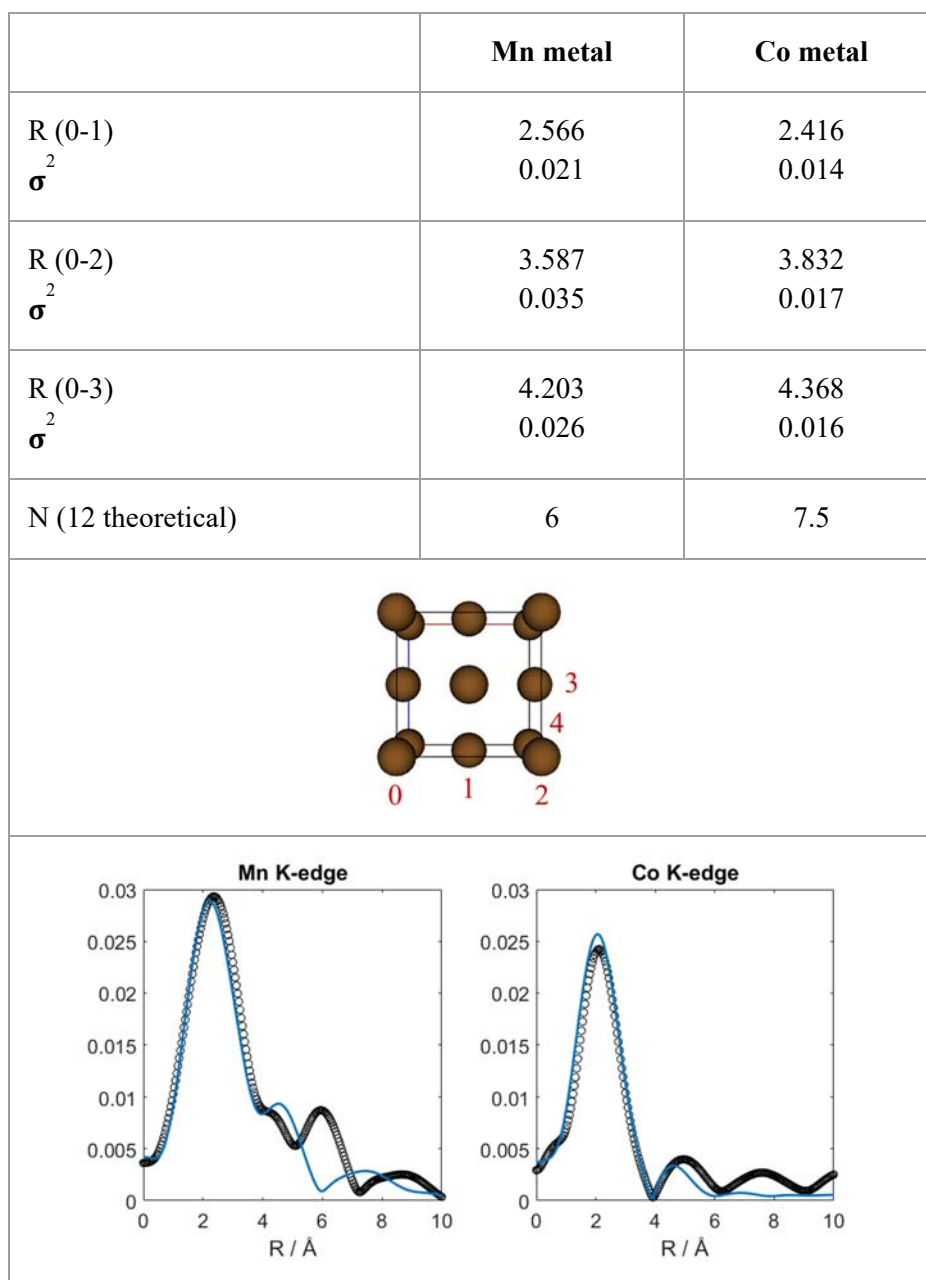


Figure S2. EXAFS analysis of the Mn and Co K-edge data obtained for the fully lithiated state of the SCMO@C-based electrode (0.01 V). The Fourier transform of the EXAFS signal matches well a fit (bottom panel), which assumes Mn metal and Co metal, respectively. As shown in the top panel, the first-shell (R0-1), the second-shell (R0-2), and the third-shell distances (R0-3) are deformed and different from the literature. This is attributed to the fact that the electrochemically formed metals in SCMO have a much higher degree of disorder than the standard references – as also confirmed by the lower average coordination number (N).

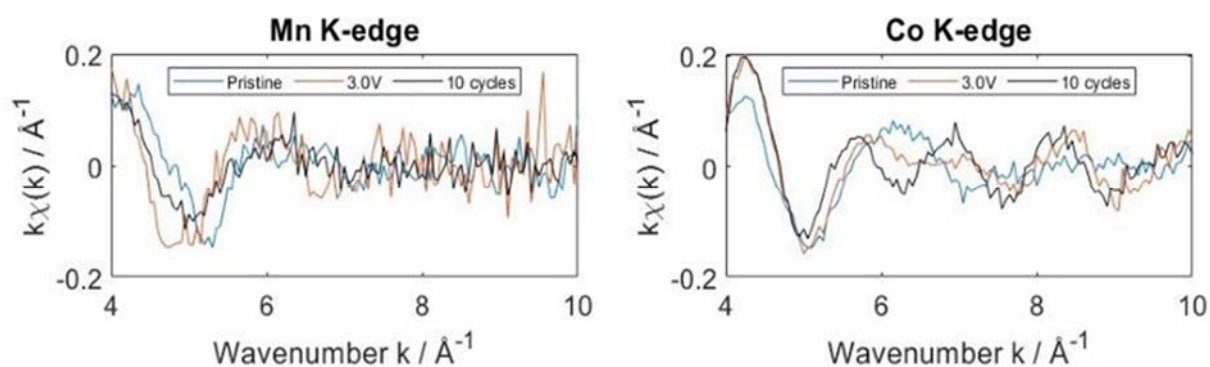


Figure S3. EXAFS signal at the Mn (left) and Co (right) K-edge for the pristine SCMO@C-based electrode and the *ex situ* samples charged to 3.0 V in the first cycle and after 10 cycles. Due to the low amount of the two TMs in the sample, the EXAFS signal is very noisy rendering any meaningful analysis of these data impossible.