

Supporting Information

Structural and Thermodynamic Understandings in Mn-Based Sodium Layered Oxides during Anionic Redox

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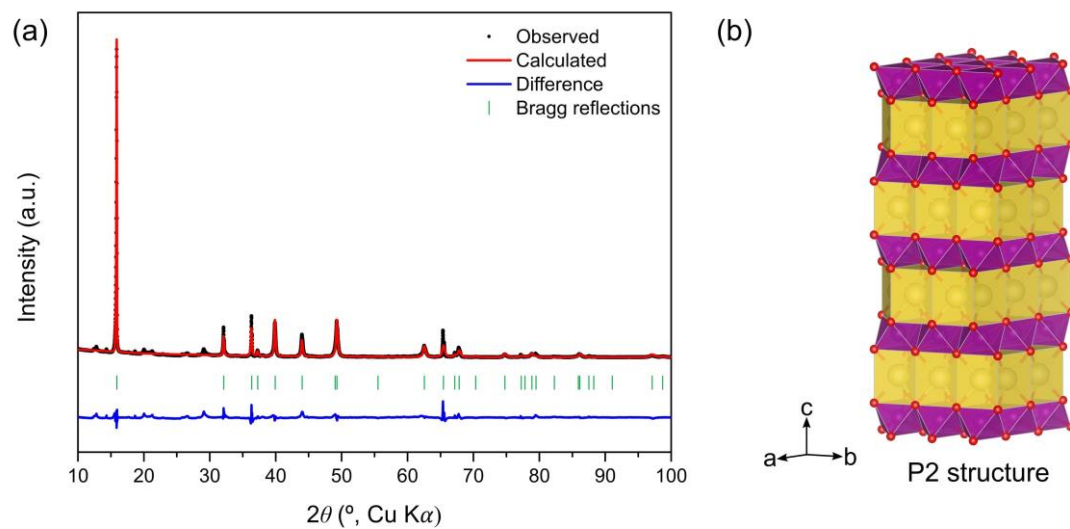


Figure S1. Structure analysis of NLMO. a) X-ray powder diffraction data for NLMO refined using b) the P2-type layered Na_xTMO₂ structure (S.G. P6₃/mmc). Rietveld refinement was carried out using GSAS software.

Table S1 Refined crystallographic parameters of NLMO from Rietveld refinement.

S. G. $P6_3/mmc$, $a = b = 2.8492(1) \text{ \AA}$, $c = 11.1372(6) \text{ \AA}$, $V = 78.298(8) \text{ \AA}^3$, $R_{wp} = 2.90\%$

Site	Mult.	x	y	Z	Occ.	U_{iso}
Mn1	2	0	0	0	0.806 ^a	0.0081(15) ^b
Li1	2	0	0	0	0.194 ^a	0.0081(15) ^b
O1	4	1/3	2/3	0.088(2)	1	0.057(15)
Na1	2	1/3	2/3	1/4	0.28(4) ^a	0.041(14) ^b
Na2	2	0	0	1/4	0.32(4) ^a	0.041(14) ^b

^aThe occupancies of Mn, Na, and Li are based on the ICP result.

^b U_{iso} values for each atom in the same layer are assumed to be equal.

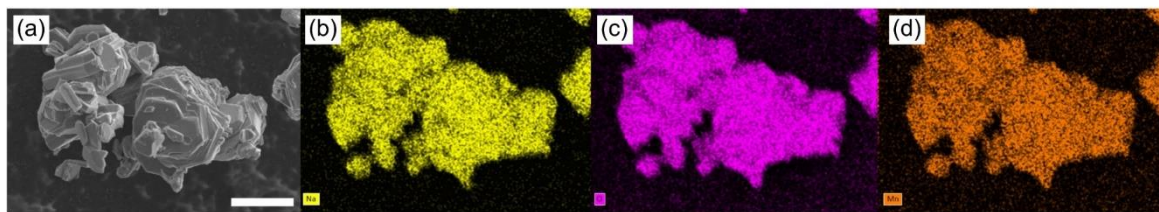


Figure S2. Morphology and elemental distributions of NLMO. a) FE-SEM image and elemental mapping of b) Na, c) O, and d) Mn for NLMO. The scale is 6 μm for all the individual images.

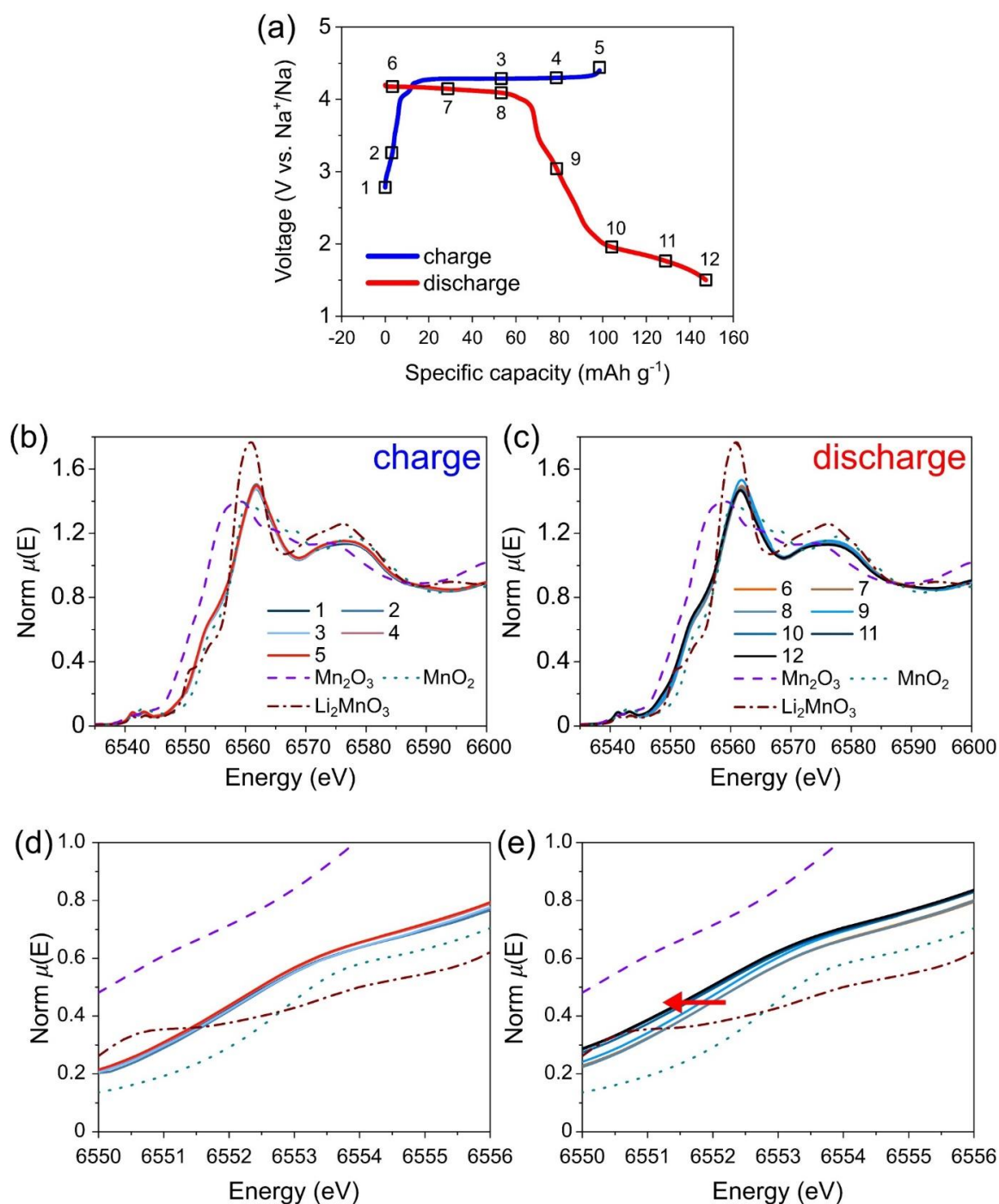


Figure S3. *In situ* XAS analysis at the Mn K-edge of NLMO during the first electrochemical cycle. a) The charge/discharge profile of Na/ NLMO cell at a rate of 30 mA g⁻¹ between 1.5 and 4.4 V during the *in situ* measurement. Evolution of the Mn K-edge XANES spectra upon b) charging and c) discharging. d,e) Enlarged spectra at the edge region corresponding to the XANES spectra of b,c), respectively. Mn K-edge XANES spectra of Mn₂O₃ (Mn³⁺), MnO₂ (Mn⁴⁺), and Li₂MnO₃ (Mn⁴⁺) are presented for reference. The numbers in Figure S3b, c, and f indicate the measurement points corresponding to those in Figure S3a.

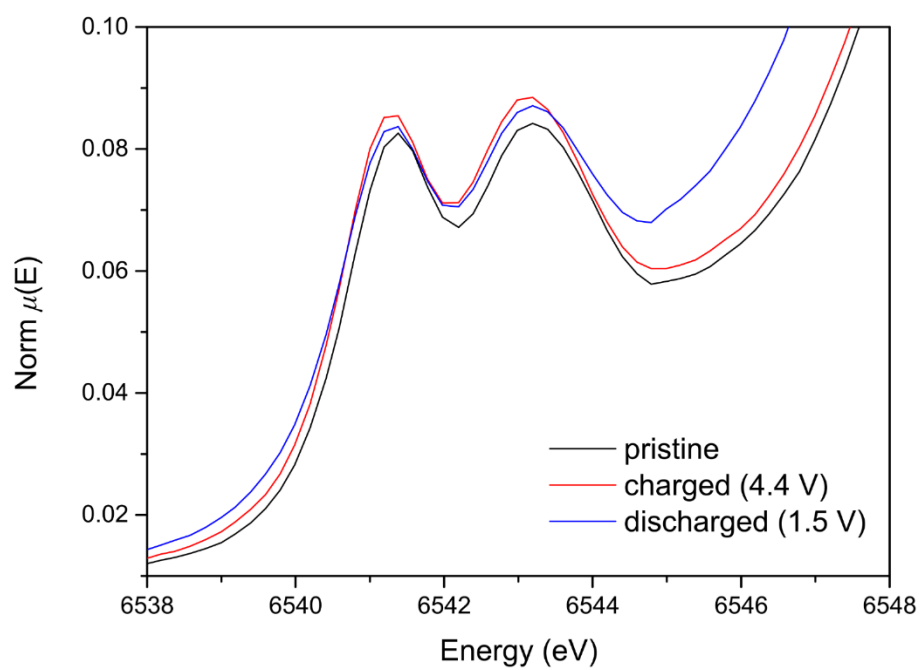


Figure S4. Comparison of the Mn K-edge pre-edge normalized XANES spectra of pristine, charged (4.4 V), and discharged (1.5 V) states of NLMO.

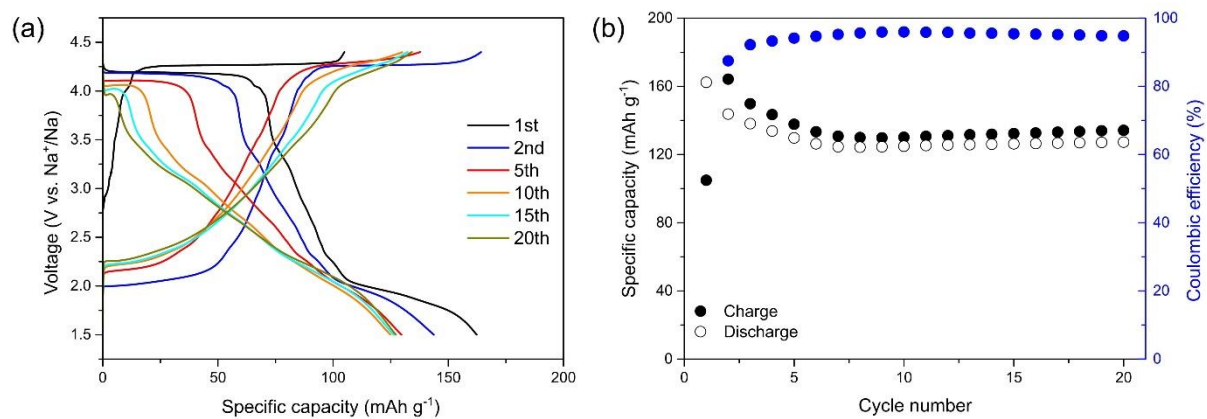


Figure S5. Electrochemical cycling performance of Na/NLMO cell. a) Charge/discharge profiles of NLMO during 20 cycles. b) Specific capacity and Coulombic efficiency of Na/NLMO cell as a function of cycle number.

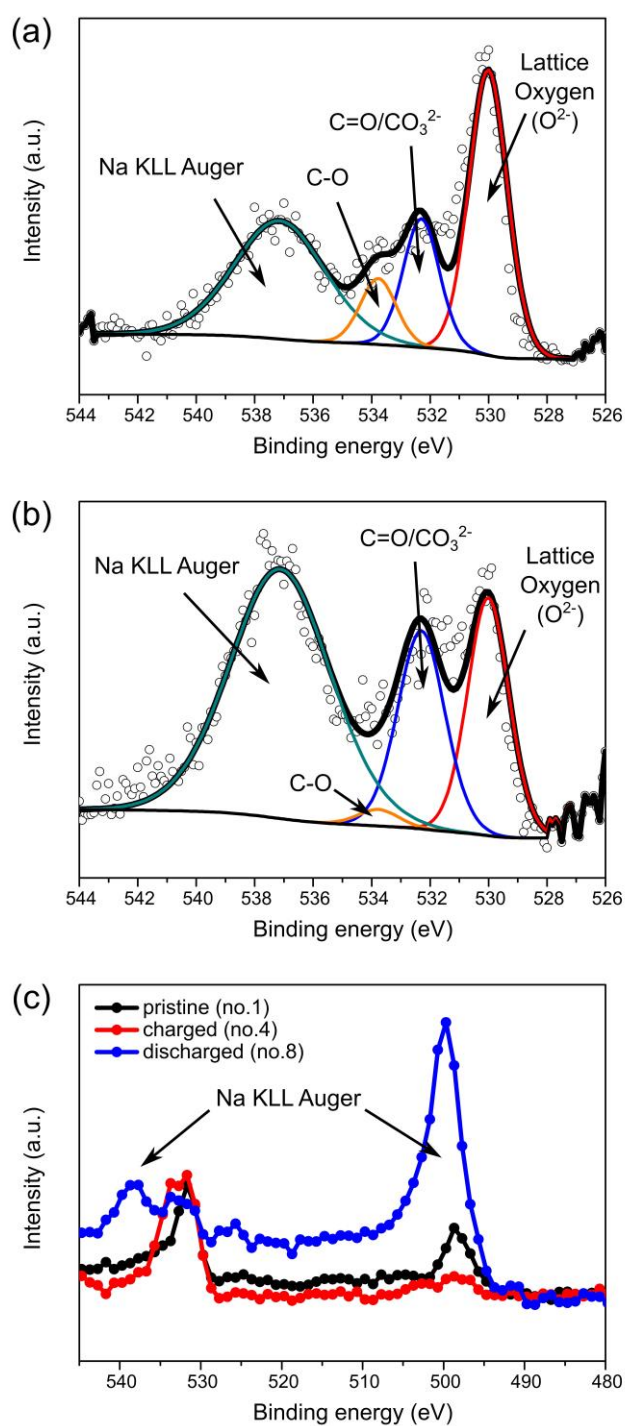


Figure S6. XPS $O1s$ peak fitting results of a) no.7 and b) no.8 states in Figure 3. c) Evolution of Na KLL Auger peaks during the first charge and discharge process.