## Supporting Information: Revisiting the Charge Compensation Mechanisms in LiNi<sub>0.8</sub>Co<sub>0.2-y</sub>Al<sub>y</sub>O<sub>2</sub> Systems

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## Supplementary Figures



Figure S1: Example extended X-ray absorption fine structure (EXAFS) fits for the a) Ni K-edge and b) Co K-edge for an NCA ( $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{Al}_{0.05}\text{O}_2$ ) 1 electrode charged to 4.75 V at 10 mA/g (vs. Li metal) with a final lithium content of x = 0.10 based on the capacity. The first Ni-O and Co-O bond lengths are extracted for each electrode from similar fits across the Ni-rich systems.



Figure S2: Surface sensitive total electron yield (TEY) measurements of the a) Ni  $L_3$ -edge and b) corresponding difference spectra between charged NCA 1 electrodes. These samples correspond to the same voltage points indicated in Fig. 2, with x = 1.00 corresponding to pristine powder, and the (C) and (D) relating to charged and discharged electrodes, respectively. The discharged electrode was charged to 4.75 V at 10 mA  $g^{-1}$ , held until the current dropped below 5 mA  $g^{-1}$ , and subsequently discharged to 2.7 V. From the difference spectra, the primary change in the Ni L<sub>3</sub>-edge lineshape is between x = 1.00 to x = 0.24, with these spectral changes matching reports of nickel 3+ to 4+ oxidation.<sup>S1,S2</sup> TEY spectra was further compared to bulk-sensitive total fluorescence yield (TFY) measurements for electrodes charged to 3.6 V (x = 0.94), 4.25 V (x = 0.17), and 4.75 V (x = 0.06) of the c) Ni L<sub>3</sub>-edge and d) Co L<sub>3</sub>-edge. For the Ni L<sub>3</sub>-edge, the bulk TFY spectra shows limited evolution between x = 0.17 and x = 0.06, with any variation relating to the presence of a Ni<sup>2+</sup> surface reduced layer at higher voltage that is prominent in the TEY spectra (shading in Fig. S2c). For the Co  $L_3$ -edge, the main peak shift to higher energy is associated with cobalt oxidation. For surface TEY and bulk TFY, the peak shifts primarily between x =0.94 and x = 0.17 indicating formal cobalt redox is primarily in this delithiation window. Combined analysis of the Ni and Co  $L_3$ -edges with TEY and TFY mode indicate limited formal nickel and cobalt oxidation at the highest degrees of delithiation.



Figure S3: a) Electrochemical profile of the first charge for LNA (LiNi<sub>0.8</sub>Al<sub>0.2</sub>O<sub>2</sub>), NCA 2, and LNC (LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>) to 4.75 V at 10 mA g<sup>-1</sup> (vs. Li metal) and room temperature (RT). Co K-edge measurements of b) NCA 2 and c) LNC. Ni K-edge measurements of d) LNA, e) NCA 2, f) LNC. The XANES Ni and Co K-edges show limited further evolution of the pre-edge and main peak beyond 4.25 V. Ni-O1 and Co-O1 bond lengths determined from EXAFS fits for g) LNA, h) NCA 2, i) LNC based on the selected voltages indicated in part a. For all three systems, the primary TM-O1 bond shortening is between 3.6 V and 4.25 V for nickel and cobalt. Combined with the XANES measurements, these measurements indicate that formal nickel and cobalt redox is primarily restricted to below ~4.25 V.



Figure S4: O K-edge partial fluorescence yield (PFY) and super partial fluorescence yield spectra (sPFY), taken between 522.9 to 524.1 eV, spectra for a) LNA, b) LNC, c) LCO (LiCoO<sub>2</sub>), and d) NCA 2 at 3.6 V, 4.25 V, and 4.75 V. The LNA and LNC measurements are compared to ground state density functional theory (DFT) calculations of corresponding Ni-rich systems with aluminum or cobalt included. In each system, most changes are upon initial delithiation and correlate with the trends in the TM oxidation from XANES and EXAFS. The Ni-rich compounds each show a similar pre-edge enhancement, which for the LNA and LNC compounds roughly matches what is expected from the ground state DFT calculations. Measurements of the O K-edge have been previously discussed for the LCO compound with the new lower excitation peaks originating from the Co<sup>4+</sup>-O 2p hybridized states.<sup>S3</sup> At higher degrees of delithiation, there are limited changes in the O K-edge spectra with only LNA and LCO showing distinct changes. As sPFY mode is sensitive to the RIXS feature, the enhancement at 531 eV in the LNA and LCO in sPFY (*shading*) can be directly related to the formation of the RIXS feature. For LNC and NCA 2, there are minimal changes in the lineshape between 4.25 V and 4.75 V. From these O K-edge measurements, the evolution of the O K-edge absorption spectra for the Ni-rich systems can be broken up into two regimes: 1) formal TM redox regime (3.6 V to 4.25 V) with pronounced changes in the O K-edge resulting from TM-O rehybridization and 2) covalency regime with limited change in absorption lineshape. For LCO, there may be continued Co contribution beyond 4.25 V resulting in further lineshape changes given its higher lithium content vs. TM at 4.25 V.



Figure S5: a) O K-edge absorption spectroscopy in PFY and sPFY mode for NCA 1 electrodes charged to 4.0 V, 4.25 V, and 4.5 V. The corresponding x values indicate the expected bulk delithiation based on charge capacity. b) O K-edge RIXS cut taken at an excitation energy of 531 eV (grey dotted line in part a). In the sPFY and RIXS cut, the difference in the spectra relating to the emergence of the weak RIXS feature at an excitation energy of 531 eV and emission energy of 523.5 eV are indicated by the arrows and shading.



Figure S6: a) First charge electrochemical profile for NCA 1 electrodes charged to 4.75 V at 10 mA g<sup>-1</sup> using either LiPF<sub>6</sub> or LiBF<sub>4</sub> as the electrolyte salt in the half-cell configuration. b) O K-edge measurements in PFY and sPFY modes for electrodes charged to 4.25 V and 4.75 V (points indicated in part a) using either the LiPF<sub>6</sub> (solid lines) or LiBF<sub>4</sub> (dotted line) electrolyte salt. The sPFY measurements show a clear peak at 531 eV related to the similar RIXS feature emergence between 4.25 V and 4.75 V. c) Comparison of highly delithiated, charged to 4.75 V, NCA 1 electrodes in quick sXAS, high throughput RIXS (htRIXS), and high resolution RIXS (hrRIXS) modes. These three modes have range of dwell times (beam exposure) using a similar flux as follows, TFY: 13 mins, htRIXS: 45 mins, and hrRIXS: 121 mins. The TEY spectra is similar between all measurements. For hrRIXS and htRIXS measurements conducted on duplicate electrodes, the sPFY spectra as a measure of the presence of the RIXS feature is similar.



Figure S7: Comparison of RIXS maps for the a) NCA 2 and b) LNC electrodes charged to 3.6 V, 4.25 V, and 4.75 V, with the corresponding lithium content indicated. The largest changes are between 3.6 V and 4.25 V, similar to the sXAS spectra, where there is a splitting of the pre-edge TM-O feature. This is related to TM-O rehybridization in the formal TM-redox regime that increases the O 2p character towards the valence band maximum. Upon further delithiation, in the covalency regime, there is limited change in the pre-edge region, no clear RIXS feature (red arrow), and a small enhancement of the elastic peak at 531 eV.



Figure S8: Comparison of RIXS maps for the a) LNA and b) LCO electrodes charged to 3.6 V, 4.25 V and 4.75 V and an electrode discharged from 4.75 V to 4.0 V, with the corresponding lithium content indicated. The largest changes in the pre-edge region are between 3.6 V and 4.25 V, similar to the sXAS spectra, where there is a splitting of the broad TM-O features. Upon further delithiation, in the covalency regime, there is the formation of the RIXS feature and a clear enhancement of the elastic peak, indicated with red arrows. For the electrode discharged to 4.0 V, there is no clear RIXS feature and the elastic peak is weakened at 531 eV.



Figure S9: a) Electrochemical profiles of disordered (DO) LNA and ordered (O) LNA electrodes charged to 4.75 V. The disordered LNA has a larger impurity phase and phase segregation compared to the ordered LNA material.<sup>S4</sup> In addition, the disordered LNA electrochemical curve has a clear high voltage plateau that is not present for the ordered compound. b) O K-edge measurements in PFY and sPFY mode for the DO and O LNA electrodes charged to 4.75 V that have a final Li-content of x = 0.2 and x = 0.24, based on the charge capacity, compared with ground state DFT calculations of  $\text{Li}_{1/16}\text{Ni}_{15/16}\text{Al}_{1/16}\text{O}_2$ . The sPFY spectra taken across the emission window of the RIXS feature for ordered and disordered LNA electrodes show a similar intensity peak at 531 eV for both systems. This comparison between ordered and disordered LNA indicates that the formation of the oxidized oxygen state in highly delithiated LNA is not dependent on the presence of a high voltage plateau in the electrochemistry.



Figure S10: Profiles of the joint X-ray and neutron powder diffraction refinement for (ab) the triclinic and (c-d) the hexagonal cells for ex-situ electrodes charged to 4.7 V versus graphite (meso carbon micro bead (MCMB)) anode. More experimental details can be found in previous works.<sup>S5,S6</sup>



Figure S11: Depth dependent XPS measurements at 0.8 keV and 6 keV of the O 1s core region for LNA conducted in tandem. The expected energy for the peroxo-like  $O_2$ )<sup>*n*-</sup> is indicated, around 1 eV above the main LNA peak. For LNA, the circled region indicates a peak at a similar binding energy of 530 eV that is related to a CEI species and not a bulk environment.

## Supplementary Tables

Table S1: Structural properties of pristine  $\text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2$  layered oxide materials. All parameters were calculated using TOPAS software from 12 hour ex-situ XRD scans (Bruker D\* Advance diffractometer, Cu K $\alpha$ ,  $\lambda = 1.5406$  Å). Based on the fitting to the rhombohedral R3m structure, we identify the initial lattice parameters, Ni/Co occupancy of the Li 3a site, and percent phase impurity in each system. Co<sub>3</sub>O<sub>4</sub> was the only impurity phase for LCO, while the two LNA samples, disordered (DO) and ordered (O), had gamma-LiAlO<sub>2</sub> as impurities. Gamma-LiAlO<sub>2</sub> commonly occurs during the fabrication of high Al-content layered oxide materials. No impurity phases were found in LNC or NCA.

Matorial	n (۱)	c (Å)	Volume $(Å^3)$	Ni/Co Occ. % Phase		р	COF
Wateria	a (A)			on 3a site	impurity	<b>IC</b> wp	GOF
LiCoO <sub>2</sub>	2.814	14.04(4)	96.308	0.00(1)	3.91	1.23	3.00
$\mathrm{LiNi}_{0.8}\mathrm{Co}_{0.2}\mathrm{O}_2\ 1$	2.868	14.17(5)	100.936	0.05(1)	0.00	2.24	4.81
${\rm LiNi}_{0.8}{\rm Co}_{0.15}{\rm Al}_{0.05}{\rm O}_2\ 1$	2.863	14.17(7)	100.598	0.01(3)	0.00	1.72	4.52
${\rm LiNi}_{0.8}{\rm Co}_{0.15}{\rm Al}_{0.05}{\rm O}_2\ 2$	2.866	14.18(0)	100.8805	0.02(5)	0.00	1.89	4.01
$LiNi_{0.8}Al_{0.2}O_2$ DO	2.873	14.20(0)	101.4894	0.08(9)	1.98	3.18	5.80
$\mathrm{LiNi}_{0.8}\mathrm{Al}_{0.2}\mathrm{O}_2~\mathrm{O}$	2.864	14.20(7)	100.9491	0.06(7)	1.30	2.67	5.74

Table S2: Comparison of Li-content for  $\text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2$  electrodes a- and c-lattice parameters and final phase for powder electrodes charged to 4.75 V at 10 mA g<sup>-1</sup> used for RIXS measurements. THe Li-content is based on the capacity. The lattice parameters given are from the in - situ XRD for tape electrodes charged at C/50 for the XRD scan at the same capacity as the electrodes used for RIXS. Of these systems, LCO undergos a phase transformation to the H1-3 staged phase.<sup>S7</sup>

Material	Li content	a (Å)/a' (Å)	c (Å)	Final phase
LCO	0.13	2.853	13.39(6)	H1-3
LNC	0.08	2.810	13.79(2)	$ m R\bar{3}m$
NCA 1	0.06	2.810	13.77(5)	$R\bar{3}m$
NCA 2	0.15	2.810	13.97(1)	$R\bar{3}m$
LNA (DO)	0.2	2.818	14.09(2)	$R\bar{3}m$

Table S3: Structure parameters of delithiated NCA 1 (charged to 4.7 V vs. graphite (MCMB) at C/20) refined simultaneously against X-ray and neutron diffraction patterns in the conventional hexagonal cell [Space group: 166 (R $\bar{3}$ m)]. The shortest O-O distance based on using a conventional hexagonal cell is found within the TM layer to be 2.4993(6) Å.

Atom type	Site	Site x		7	Occupancy	Atomic displacement parameters $(\mathring{A}^2)$		
(charge)	5100	11	J	L	e coupairoj	$\mathbf{U}_{11} = \mathbf{U}_{22}$	$\mathbf{U}_{33}$	
Li	3b	0	0	0.5	0.077(5)		$U_{iso} = 0.0127$	
Ni (+3)	3b	0	0	0.5	0.0145(4)		$U_{iso} = 0.0127$	
Ni (+3)	3a	0	0	0	0.7855(4)	0.00443(7)	0.0202(2)	
Co (+3)	3a	0	0	0	0.15	0.00443(7)	0.0202(2)	
Al (+3)	3a	0	0	0	0.05	0.00443(7)	0.0202(2)	
Li	3a	0	0	0	0.0145(4)		$U_{iso} = 0.0127$	
O (-2)	6c	0	0	0.26457(3)	1	0.0067(1)	0.0163(3)	

The O-O bond distance in M-O layer: 2.5010(7) Å, 2.808986(9) Å

 $^{*}U_{12} = U_{11}/2$ 

Cell parameters:

 $a=b=2.808986(9) {\rm \AA}, c=13.8437(1) {\rm \AA}, \alpha=\beta=90^{\circ}, \gamma=120^{\circ}$ 

 $R_{wp} = 5.71\%, R_{exp} = 3.73\%$ 

Table S4: Structure parameters of delithiated NCA 1 (charged to 4.7 V vs. graphite (MCMB) at C/20) refined simultaneously against X-ray and neutron diffraction patterns in the low-symmetry triclinic cell [Space Group: 2 (P $\overline{1}$ )]. The shortest O-O distance based on using a low-symmetry triclinc cell is found within the TM layer to be 2.468(4) Å

Atom type (charge)	Site	x	У	z	Occupancy	Atomic displacement parameters $(Å^2)$		
						$\mathbf{U}_{11} = \mathbf{U}_{22}$	$\mathbf{U}_{33}$	$\mathbf{U}_{13} = \mathbf{U}_{23}$
Li	1a	0	0	0	0.105(5)		$U_{iso} = 0.012$	27
Ni (+3)	1a	0	0	0	0.0130(4)		$U_{iso} = 0.012$	27
Ni (+3)	$1\mathrm{h}$	0.5	0.5	0.5	0.7870(4)	0.0034(1)	0.0221(2)	-0.0021(2)
Co (+3)	$1\mathrm{h}$	0.5	0.5	0.5	0.15	0.0034(1)	0.0221(2)	-0.0021(2)
Al (+3)	$1\mathrm{h}$	0.5	0.5	0.5	0.05	0.0034(1)	0.0221(2)	-0.0021(2)
Li	$1\mathrm{h}$	0.5	0.5	0.5	0.0130(4)		$U_{iso} = 0.012$	27
O (-2)	2i	0.762(1)	0.758(1)	0.7055(1)	1	0.0019(1)	0.0215(5)	-0.0041(2)

The O-O bond distance in M-O layer: 2.473(4) Å, 2.488(4) Å, 2.809004(9) Å

 $^*\mathrm{U}_{12}$  was fixed to 0 when an isotropic ADPs were refined

Cell parameters:

 $a=b=2.809000(9) \mathring{A}, c=4.89130(4) \mathring{A}, \alpha=\beta=73.3130(1)^{\circ}, \gamma=60^{\circ}$ 

The Corresponding hexagonal cell parameters:

 $a=b=2.809000(9) \mathring{A}, c=13.8439(1) \mathring{A}, \alpha=\beta=90^\circ, \gamma=120^\circ$ 

 $R_{wp} = 5.70\%, R_{exp} = 3.73\%$ 

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