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Hysteresis Induced by Incomplete Cationic Redox in Li-Rich 3d-Transition-Metal Layered Oxides Cathodes

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Supporting Information

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Figure S1. Scanning electron microscopy (SEM) images and dispersive X-ray spectroscopy (EDS) results of a) NM26 and b) NM44. Scale bar, 1 µm.
Figure S2. Field emission transmission electron microscopy (FE-TEM) and dispersive X-ray spectroscopy (EDS) mapping images of a) NM26 and b) NM44. Scale bar, 100 nm.

Figure S3. Charge-discharge curves of a) NM26 and b) NM44 with fixed 2.5 V discharge cut-off voltage and gradually opened charge cut-off voltage from 3.7 to 4.8 V at 30 mA g\(^{-1}\). Charge-discharge curves of c) NM26 and d) NM44 with fixed 4.8 V charge cut-off voltage and gradually decreased discharge cut-off voltage from 4.5 to 2.5 V at 30 mA g\(^{-1}\).
Figure S4. Variation of Ni K-edge white-line peak during the charge a) and discharge b) process. Variation of Ni K-edge half-height energy Ni during charge c) and discharge d) process.
Figure S5. Variation of Ni K-edge white-line peak energy a) and half-height energy b) during the first cycle charge-discharge process.

Figure S6. Extended X-ray absorption fine structure (EXAFS) fitting curves for Ni in NM44 at different charge-discharge states.
**Figure S7.** Extended X-ray absorption fine structure (EXAFS) fitting curves for Mn in NM44 at different charge-discharge states.

**Figure S8.** Mn to Oxygen bond length variation in NM44 during first cycle charge-discharge process.

**Figure S9.** Mn L-edge soft XAS spectra of NM26 at different charge-discharge states.
Figure S10. a) Single-step schematic diagram of a galvanostatic intermittent titration technique (GITT) experiment at 4.01 V on charging for NM44; b) GITT curves at 4.01 V during discharge process; c) GITT curves at 3.40 V during the discharge process.
| **Table S1.** Rietveld refinement results of pristine Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Crystal system** | Rhombohedral |
| **Space group** | R -3m (166) |
| **a = 2.8606(5) Å** | **c = 14.254(2) Å** | **Volume = 100.01(3)** |
| **R_wp = 7.97%** | **R_bragg = 2.27%** |
| **Atom** | **Site** | **x** | **y** | **z** | **Occ** | **B value** |
| Li(1)/Ni(1) | 3b | 0 | 0 | 0.5 | 0.962(1)/0.038(1) | 1.36(7) |
| Li(2)/Ni(2)/Mn(2) | 3a | 0 | 0 | 0 | 0.238(1)/0.162(1)/0.219(1) | 0.219(1) |
| O1 | 6c | 0 | 0 | 0.25715(6) | 1 | 0.89(2) |

Composition from ICP-OES: Li$_{1.20(1)}$Ni$_{0.20(1)}$Mn$_{0.60(1)}$O$_2$

| **Table S2.** Rietveld refinement results of pristine Li$_{1.2}$Ni$_{0.4}$Mn$_{0.4}$O$_2$. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Crystal system** | Rhombohedral |
| **Space group** | R -3m (166) |
| **a = 2.8639(3) Å** | **c = 14.246(1) Å** | **Volume = 100.19(2)** |
| **R_wp = 6.94%** | **R_bragg = 2.00%** |
| **Atom** | **Site** | **x** | **y** | **z** | **Occ** | **B value** |
| Li(1)/Ni(1) | 3b | 0 | 0 | 0.5 | 0.980(1)/0.020(1) | 0.65(6) |
| Li(2)/Ni(2)/Mn(2) | 3a | 0 | 0 | 0 | 0.220(1)/0.380(1)/0.319(8) | 0.319(8) |
| O1 | 6c | 0 | 0 | 0.25783(6) | 1 | 1.17(2) |

Composition from ICP-OES: Li$_{1.19(1)}$Ni$_{0.40(1)}$Mn$_{0.40(1)}$O$_2$
### Table S3. Linear combination fitting results of Ni XANES spectra.

| Sample | Ni2+(weight) | error | 10(Ni4+)(weight) | error | Ni oxidation state | error |
|--------|-------------|-------|------------------|-------|-------------------|-------|
| Ni^{2+} | 1           | 0     | 0                | 0     | 2                 | 0     |
| 1      | 0.526514    | 0.011271 | 0.473486 | 0.011271 | 2.946973 | 0.067629 |
| 2      | 0.463692    | 0.010934 | 0.536308 | 0.010934 | 3.072617 | 0.065603 |
| 3      | 0.365388    | 0.010717 | 0.634612 | 0.010717 | 3.269225 | 0.0643 |
| 4      | 0.287362    | 0.009755 | 0.712638 | 0.009755 | 3.425725 | 0.058532 |
| 5      | 0.16417     | 0.007824 | 0.83583  | 0.007824 | 3.671659 | 0.046943 |
| 6      | 0.095521    | 0.00584  | 0.904479 | 0.00584  | 3.808957 | 0.035043 |
| 7      | 0.065822    | 0.004517 | 0.998138 | 0.004517 | 3.996276 | 0.058999 |
| 8      | 0.013222    | 0.002699 | 0.986778 | 0.002699 | 3.973556 | 0.016194 |
| 9      | 0.001862    | 0.001166 | 1         | 0     | 4                 | 0     |
| 10     | 0           | 0     | 1                | 0     | 4                 | 0     |
| 11     | 0.019734    | 0.001417 | 0.980266 | 0.001417 | 3.960533 | 0.0085 |
| 12     | 0.046654    | 0.002121 | 0.953346 | 0.002121 | 3.90691  | 0.02729 |
| 13     | 0.054368    | 0.004281 | 0.945632 | 0.004281 | 3.891264 | 0.025686 |
| 14     | 0.10518     | 0.004733 | 0.89482  | 0.004733 | 3.78964  | 0.028398 |
| 15     | 0.056664    | 0.002275 | 0.943336 | 0.002275 | 3.886673 | 0.01365 |
| 16     | 0.091481    | 0.003891 | 0.908519 | 0.003891 | 3.817037 | 0.023347 |
| 17     | 0.13517     | 0.004646 | 0.86483  | 0.004646 | 3.729661 | 0.027876 |
| 18     | 0.150068    | 0.004052 | 0.849932 | 0.004052 | 3.699863 | 0.024315 |
| 19     | 0.170221    | 0.004031 | 0.829779 | 0.004031 | 3.659558 | 0.024187 |
| 20     | 0.213489    | 0.004664 | 0.786511 | 0.004664 | 3.573021 | 0.027984 |
| 21     | 0.280582    | 0.00568  | 0.719418 | 0.00568  | 3.438836 | 0.034079 |
| 22     | 0.360193    | 0.006427 | 0.639807 | 0.006427 | 3.279614 | 0.038563 |
| 23     | 0.43864     | 0.006918 | 0.56136  | 0.006918 | 3.12272  | 0.04151 |
| 24     | 0.533887    | 0.006701 | 0.466113 | 0.006701 | 2.932226 | 0.040206 |
| 25     | 0.625396    | 0.00638  | 0.374604 | 0.00638  | 2.749209 | 0.038277 |
| 26     | 0.657628    | 0.00695  | 0.342372 | 0.00695  | 2.684744 | 0.0417 |
| 27     | 0.735588    | 0.005607 | 0.264412 | 0.005607 | 2.528825 | 0.033644 |
| 28     | 0.756454    | 0.005404 | 0.243546 | 0.005404 | 2.487091 | 0.032422 |

### Table S4. EXAFS analysis parameters and R factor of Ni and Mn for NM44 at different charge-discharge states.

| Element | Ni(set1) | Ni(set2) | Mn       |
|---------|----------|----------|----------|
| Independent points | 197.11 | 160.33 | 55.94 |
| Number of variables | 80 | 65 | 26 |
| Chi-square | 474849.60 | 693736.08 | 111378.92 |
| Reduced chi-square | 4054.78 | 7277.35 | 3720.38 |
Table S5. EXAFS analysis results of Ni for NM44 at different charge-discharge states (set1).

| Ni   | S0²  | ΔE₀ (eV) | Scattering path | CN | σ² (Å²) | R_{eff} (Å) | R (Å) |
|------|------|----------|----------------|----|---------|-------------|-------|
| 1    | 0.9  | -0.777   | Ni-O           | 6  | 113(2)  | 1.9199      | 2.037(10) |
|      |      |          | Ni-M           | 6  | 61(1)   | 2.8154      | 2.871(6)  |
| 2    | 0.9  | -0.957   | Ni-O           | 6  | 109(1)  | 1.9199      | 2.018(13) |
|      |      |          | Ni-M           | 6  | 60(1)   | 2.8154      | 2.863(8)  |
| 3    | 0.9  | -1.196   | Ni-O           | 6  | 107(1)  | 1.9199      | 2.003(15) |
|      |      |          | Ni-M           | 6  | 58(1)   | 2.8154      | 2.857(10) |
| 4    | 0.9  | -1.308   | Ni-O           | 6  | 98(1)   | 1.9199      | 1.984(9)  |
|      |      |          | Ni-M           | 6  | 59(1)   | 2.8154      | 2.847(6)  |
| 5    | 0.9  | -1.058   | Ni-O           | 6  | 80(1)   | 1.9199      | 1.978(11) |
|      |      |          | Ni-M           | 6  | 58(1)   | 2.8154      | 2.844(8)  |
| 6    | 0.9  | -1.067   | Ni-O           | 6  | 74(1)   | 1.9199      | 1.972(11) |
|      |      |          | Ni-M           | 6  | 60(1)   | 2.8154      | 2.841(8)  |
| 7    | 0.9  | -1.179   | Ni-O           | 6  | 69(1)   | 1.9199      | 1.967(7)  |
|      |      |          | Ni-M           | 6  | 59(1)   | 2.8154      | 2.838(6)  |
| 8    | 0.9  | -1.287   | Ni-O           | 6  | 61(1)   | 1.9199      | 1.964(8)  |
|      |      |          | Ni-M           | 6  | 59(1)   | 2.8154      | 2.837(6)  |
| 9    | 0.9  | -1.174   | Ni-O           | 6  | 59(1)   | 1.9199      | 1.965(9)  |
|      |      |          | Ni-M           | 6  | 59(1)   | 2.8154      | 2.837(7)  |
| 10   | 0.9  | -1.561   | Ni-O           | 6  | 61(1)   | 1.9199      | 1.964(6)  |
|      |      |          | Ni-M           | 6  | 58(1)   | 2.8154      | 2.836(4)  |
| 11   | 0.9  | -1.698   | Ni-O           | 6  | 63(1)   | 1.9199      | 1.965(6)  |
|      |      |          | Ni-M           | 6  | 58(1)   | 2.8154      | 2.838(5)  |
| 12   | 0.9  | -1.900   | Ni-O           | 6  | 66(1)   | 1.9199      | 1.966(4)  |
|      |      |          | Ni-M           | 6  | 60(1)   | 2.8154      | 2.838(3)  |
| 13   | 0.9  | -1.551   | Ni-O           | 6  | 76(4)   | 1.9199      | 1.972(3)  |
|      |      |          | Ni-M           | 6  | 64(3)   | 2.8154      | 2.840(3)  |
| 14   | 0.9  | -1.811   | Ni-O           | 6  | 69(3)   | 1.9199      | 1.966(3)  |
|      |      |          | Ni-M           | 6  | 60(2)   | 2.8154      | 2.836(3)  |
| 15   | 0.9  | -2.046   | Ni-O           | 6  | 68(1)   | 1.9199      | 1.968(3)  |
|      |      |          | Ni-M           | 6  | 61(1)   | 2.8154      | 2.838(3)  |
| 16   | 0.9  | -2.006   | Ni-O           | 6  | 73(2)   | 1.9199      | 2.037(15) |
|      |      |          | Ni-M           | 6  | 63(1)   | 2.8154      | 2.871(12) |
Table S6. EXAFS analysis results of Ni for NM44 at different charge-discharge states (set2).

|   | S0^2 | ΔE_0 (eV) | Scattering path | CN | σ^2 (×10^{-4} Å^2) | R_eff (Å) | R (Å) |
|---|------|----------|----------------|----|---------------------|-----------|-------|
| 17 | 0.9  | -2.331   | Ni-O           | 6  | 74(18)              | 1.9199    | 1.891(19) |
|    |      |          | Ni-M           | 6  | 65(11)              | 2.8154    | 2.839(14) |
| 18 | 0.9  | -2.040   | Ni-O           | 6  | 82(10)              | 1.9199    | 1.896(10) |
|    |      |          | Ni-M           | 6  | 65(6)               | 2.8154    | 2.842(8)  |
| 19 | 0.9  | -1.928   | Ni-O           | 6  | 83(10)              | 1.9199    | 1.899(10) |
|    |      |          | Ni-M           | 6  | 66(6)               | 2.8154    | 2.845(8)  |
| 20 | 0.9  | -2.104   | Ni-O           | 6  | 90(9)               | 1.9199    | 1.905(9)  |
|    |      |          | Ni-M           | 6  | 66(5)               | 2.8154    | 2.846(7)  |
| 21 | 0.9  | -1.892   | Ni-O           | 6  | 96(10)              | 1.9199    | 1.917(10) |
|    |      |          | Ni-M           | 6  | 66(5)               | 2.8154    | 2.854(7)  |
| 22 | 0.9  | -1.86162 | Ni-O           | 6  | 105(14)             | 1.9199    | 1.930(13) |
|    |      |          | Ni-M           | 6  | 64(6)               | 2.8154    | 2.860(8)  |
| 23 | 0.9  | -1.46826 | Ni-O           | 6  | 112(18)             | 1.9199    | 1.949(17) |
|    |      |          | Ni-M           | 6  | 64(7)               | 2.8154    | 2.868(11) |
| 24 | 0.9  | -2.47884 | Ni-O           | 6  | 118(21)             | 1.9199    | 1.969(20) |
|    |      |          | Ni-M           | 6  | 63(8)               | 2.8154    | 2.878(13) |
| 25 | 0.9  | -0.85065 | Ni-O           | 6  | 109(17)             | 1.9199    | 1.989(17) |
|    |      |          | Ni-M           | 6  | 63(7)               | 2.8154    | 2.885(10) |
| 26 | 0.9  | -0.53461 | Ni-O           | 6  | 107(20)             | 1.9199    | 1.997(20) |
|    |      |          | Ni-M           | 6  | 61(9)               | 2.8154    | 2.888(13) |
| 27 | 0.9  | -0.56973 | Ni-O           | 6  | 99(15)              | 1.9199    | 2.010(15) |
|    |      |          | Ni-M           | 6  | 62(6)               | 2.8154    | 2.895(10) |
| 28 | 0.9  | -0.48658 | Ni-O           | 6  | 98(17)              | 1.9199    | 2.014(17) |
|    |      |          | Ni-M           | 6  | 60(7)               | 2.8154    | 2.896(11) |
| Ni^{2+} | 0.9 | -0.54082 | Ni-O           | 6  | 53(11)              | 1.9199    | 2.047(12) |
|      |      |          | Ni-M           | 6  | 53(6)               | 2.8154    | 2.908(9)  |
### Table S7. EXAFS analysis results of Mn for NM44 at different charge-discharge states.

| Mn  | $S_0^+$ | $\Delta E_0$ (eV) | Scattering path | CN  | $\sigma^2$ ($\times 10^{-4}$ Å$^2$) | $R_{\text{eff}}$ (Å) | R (Å)  |
|-----|---------|-------------------|------------------|-----|-----------------------------------|-----------------------|--------|
| Pristine | 0.721 | 2.405 | Mn-O | 6 | 23(8) | 1.9199 | 1.897(7) |
|  |  |  | Mn-M | 3 | 14(8) | 2.8154 | 2.885(8) |
| C4.3V | 0.721 | 1.176 | Mn-O | 6 | 36(9) | 1.9199 | 1.882(9) |
|  |  |  | Mn-M | 3 | 22(9) | 2.8154 | 2.855(9) |
| C4.8V | 0.721 | 0.519 | Mn-O | 6 | 51(12) | 1.9199 | 1.879(12) |
|  |  |  | Mn-M | 3 | 21(10) | 2.8154 | 2.865(12) |
| D3.62V | 0.721 | 1.213 | Mn-O | 6 | 36(9) | 1.9199 | 1.887(9) |
|  |  |  | Mn-M | 3 | 15(8) | 2.8154 | 2.878(9) |
| D2.5V | 0.721 | 0.954 | Mn-O | 6 | 46(11) | 1.9199 | 1.893(11) |
|  |  |  | Mn-M | 3 | 14(9) | 2.8154 | 2.899(10) |

References

[1] B. Ravel, M. Newville, *Journal of Synchrotron Radiation* **2005**, *12*, 537.