Correlating Cation Ordering and Voltage Fade in a Lithium-Manganese-Rich Lithium-Ion Battery Cathode Oxide: a Joint Magnetic Susceptibility and TEM Study

Debasish Mohanty,[a]* Athena S. Sefat,[a] Jianlin Li,[b] Roberta A. Meisner,[a] Adam J. Rondinone,[c] E. Andrew Payzant,[d] Daniel P. Abraham,[e] David L. Wood III,[b] and Claus Daniel[b,f,]*

[a]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37931, USA [b]Energy and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA [c]Center for Nanophase Materials Sciences , Oak Ridge National Laboratory, Oak Ridge, TN 37931, USA[d]Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, T 37831, USA [e]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, USA [f]Bredesen Center for Interdisciplinary Research and Graduate Education, University of Tennessee, Knoxville, TN 37996, USA.

Supplementary Information

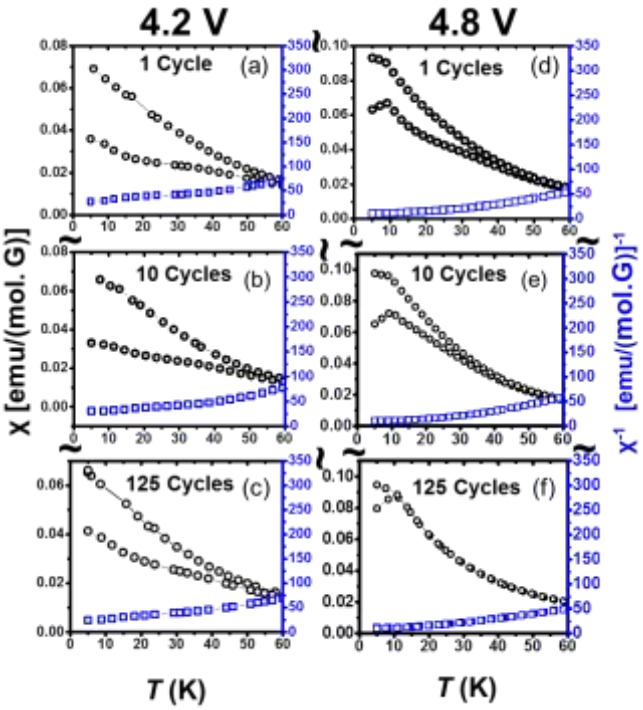

Figure S1: Temperature dependence of the molar magnetic susceptibility in the temperature region 5K-60K of cycled LMR-NMC when cycled at a cutoff voltage 4.2V (a-c) and 4.8V (d-f). During 4.2V cycling the bifurcation of FC and ZFC can be observed after I cycle (a), 10 cycles(b), and after 125 cycles (c). However, while cycling at 4.8V, the bifurcation of FC and ZFC suppress after subsequent 1 and 10 cycles (d-e) and vanishes after 125 cycles (f).

Table TS1: magnetic moments of Mn, Co, and Ni at different oxidation states and in low-spin (LS), and high-spin (HS) configurations

	Ni^{2+} HS/LS	Ni^{3+} HS	Ni^{3+} LS	Co^{3+} HS	Co^{3+} LS	Co^{4+} HS	Co^{4+} LS	Ni^{4+} HS	Ni^{4} LS	Mn^{3+} HS	Mn^{3+} LS	Mn^{4+} HS/LS	Mn^{5+} HS/LS	Mn^{6+} LS	Mn^{2+} LS	Mn^{2+} HS
Number of unpaired electrons (n)	2	3	**1**	4	0	5	1	4	0	4	2	3	2	1	1	5
Spin-only magnetic moment (μ_S) B.M.	2.8	3.9	**1.7**	4.9	0	5.9	1.7	4.9	0	4.9	2.8	3.9	2.8	1.7	1.7	5.9

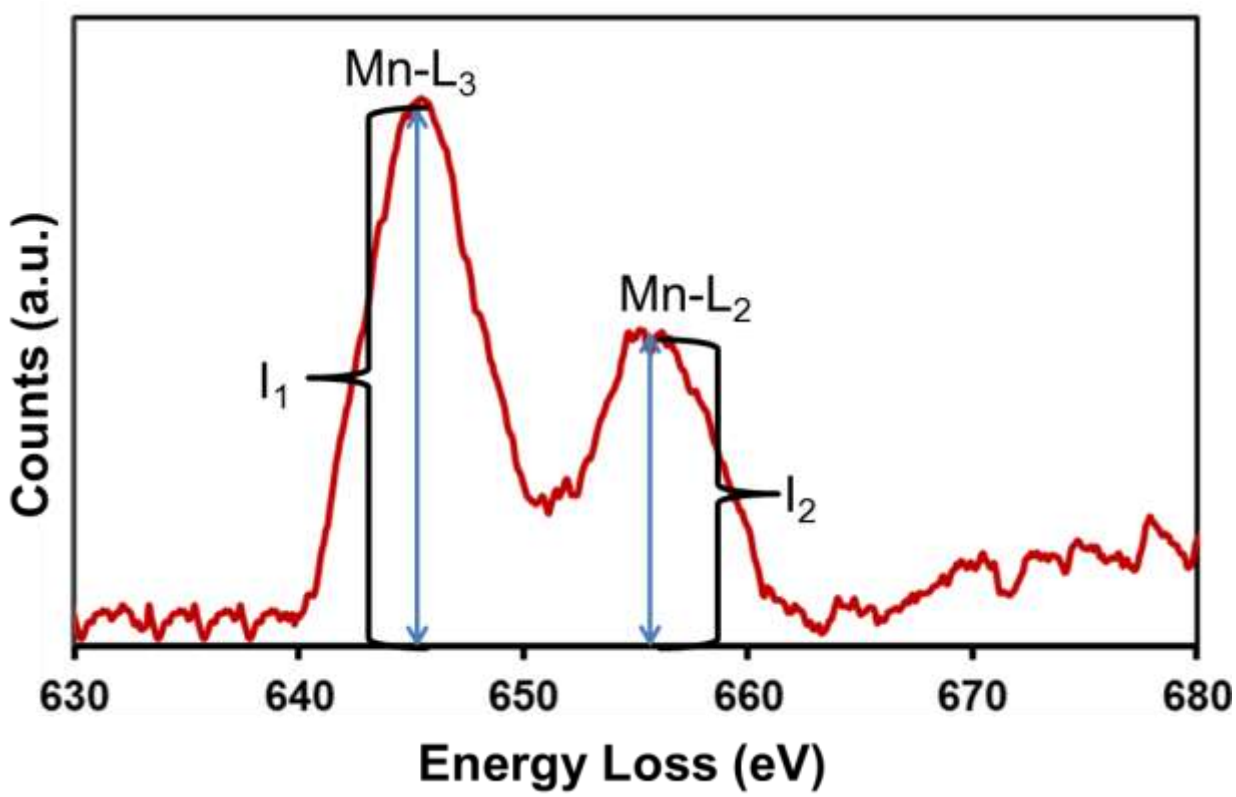

Figure S2: EELS spectra collected from the pristine LMR-NMC cathode oxide. The Mn L_3/L_2 ratio was calculated as I_1/I_2. Where I_1 is the intensity of Mn-L_3 and I_2 is the intensity of Mn-L_2 white lines. This procedure was adopted to calculate the L_3/L_2 ratio for all the materials.