Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

Thermodynamic and Kinetic Studies of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ as a Positive Electrode Material for Li-ion Batteries using First Principles

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S1. Computational Methods:

In order to predict the cationic ordering in the metal layers, we adopted a funneled strategy. According to this strategy, we initially performed screening of a large number of possible cationic configurations using a classical energy potential. Subsequently, the top-scoring candidates were rescored using DFT. All the calculations were performed with 5 × 4 supercells with 60 formula units of R3m (α-$NaFeO_2$ type) layered structure. All the atomistic classical calculations were performed using the GULP code.[1] The interactions were modeled by two components: long range electrostatic interactions and short-range repulsive and van der Walls interactions. The Buckingham potentials were used to model the non-bonded interactions. Specifically, the Buckingham potential parameters for Co^{+2}, Li^{+} and O^{2-} were taken from the work of Islam et al.[2] on olivine phosphates and that of Mn^{+4} were adopted from the recent work of Park et al. on NCM-333.[3] The effect of electronic polarization was added using a core-shell model.[4, 5] The potentials and core-shell charges are given in Table S1.

The Vienna ab-initio simulation package[6-9] (VASP) was used to perform all DFT calculations, and these calculations employed the generalized gradient approximation (GGA) and GGA+U functionals.[10] Specifically, we employed the PBE[11] exchange-correlation functional. Two sets of U values were taken from previous studies[12, 13] on similar class of materials for Ni, Co and Mn, U = 5.96, 5.00 and 5.10 eV and U' = 6.40, 3.30 and 3.40 eV, respectively. Two different set of U values were taken to understand the effect of different U values on electrochemical properties of this materials. The plane-wave projector augmented wave[12] (PAW) based pseudo-potential method was employed. Spin-polarized DFT, with antiferromagnetic spin ordering,[13-15] was used to relax all structures. The kinetic energy cutoff was chosen to be 520 eV. Due to the very large super-cell, the calculations were performed using the Monkhorst Pack scheme with a mesh of 2×2×1 k-points. To incorporate the effect of dispersion, we employed DFT+D3 method and optPBE-vdW as implemented in the VASP code.[16-18] Li diffusion barriers were calculated using the nudged elastic band (NEB)[19] method in the fully intercalated limit with gamma k-point only, and a 400 eV kinetic energy cutoff was used. NEB calculations were carried out with the standard GGA functional (without U) to avoid mixing of the diffusion barrier with a charge transfer barrier.[20] The lattice parameters for defect structures were fixed at the relaxed lattice parameters obtained by the GGA+U calculations. We note that dispersion corrections become important in the low lithiation limit. Since the Li diffusion barriers are calculated at the fully lithiated limit, dispersion corrections were not included in the NEB calculations.

S2. Experimental methods

Electrochemical tests were carried out in two-electrode cells of a 2325 coin-type configuration. The working electrodes were composites of a mixture of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ material, carbon black and polyvinylidendifluoride binder (80:10:10 by weight) on aluminum foil. We used polypropylene separator from Celgard, Inc. and electrolyte solutions (high purity, Li battery grade) comprising ethyl-methyl carbonate and ethylene carbonate (weight ratio of 7:3) and 1M $LiPF_6$. The content of hydrofluoric acid and water in solutions was not more than 30 ppm and 10 ppm, respectively. Electrochemical cells were assembled in glove boxes filled with highly pure argon (VAC, Inc.). After assembling, the electrochemical cells were stored at room temperature for 24 h to ensure a complete impregnation of the electrodes and the separators with the electrolyte solution. The electrochemical measurements were performed using a multichannel battery tester from Maccor, Inc., model 2000. For testing, we used a constant current mode in the potential range of 2.7 – 4. 3 V.

Table S1. Buckingham Potential parameter and Core-Shell Interaction for $LiNi_{0.50}Co_{0.2}Mn_{0.3}O_2$.

Buckingham Potentials			
Interaction	A (eV)	ρ (Å)	C (eV-Å^6)
$^aLi^+$--O^{2-}	632.10	0.2906	0.0
$^bNi^{+2}$--O^{2-}	683.5	0.3332	0.0
$^bNi^{+3}$--O^{-2}	954.1969	0.3336	0.0
$^cNi^{+2.4}$--O^{2-}	791.77876	0.0.33336	0.0
$^aCo^{+3}$--O^{2-}	1329.82	0.3087	0.0
$^cMn^{+4}$--O^{2-}	1397.63	0.3211	0.0
$^aO^{2-}$--O^{2-}	22764.3	0.149	65.0
Core-Shell Interaction			
Interactions	Y (e)		K (eV.Å^{-2})
$^aLi^+$	1.0		9999.0
$^bNi^{+2}$	2.0		8.77
$^bNi^{+3}$	3.0		8.77
$^cNi^{+2.4}$	2.4		8.77
$^aCo^{+3}$	2.04		196.3
$^cMn^{+4}$	4.0		95.0
$^aO^{2-}$	-2.96		65.0

[a]Parameters adopted from ref [21]
[b]Parameters adopted from ref [22]

[c]Parameters adopted from ref [3]
[c]As the unit cell contains 18 Ni^{+2} ions and 12 Ni^{+3} ions, the Ni ions are treated using +2.4 average charge. The values of all the $Ni^{+2.4}$ parameters were calculated by weighted average of the parameters of Ni^{+3} and Ni^{+2} (60% of Ni^{+2} and 40% of Ni^{+3}).

Table S2. Experimental lattice parameters and structural parameters for structures with the most stable cationic ordering using atomistic simulation, DFT-GGA, DFT and GGA+U+D3.

	a	*c*	*a*	*c*	*a*	*c*	*a*	*c*
	Atomistic		GGA		GGA+U+D3		Exp. [a]	
x=1.00	2.87	14.21	2.89	14.29	2.86	14.16	2.86	14.21

Distance (Å)[a]	Atomistic	GGA	GGA+U+D3
Ni-O	1.92, 2.02, 2.01, 2.01, 2.03, 1.96	2.051, 2.074, 2.062, 2.058, 2.087,2.073	2.039, 2.063, 2.060, 2.031, 2.065, 2.045
Mn-O	1.86, 1.86, 1.85, 1.86, 1.87, 1.85	1.874, 1.970, 1.933, 1.942, 1.995, 1.885	1.941,1.983,1.885,1.880, 1.958, 1.936
Co-O	1.92, 1.92,1.94, 1.93, 1.94, 1.92	1.919, 1.933, 1.955, 1.911, 1.955, 1.938	1.914, 1.921, 1.945, 1.917, 1.952, 1.931

[a] Distances are reported for the same octahedral configurations optimized with different methods.

Table S3. Integrated DOS (up to Fermi level) of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ using GGA and GGA+U.

Ion	Integrated DOS (GGA+U)	Integrated DOS (GGA)

Ni^{+2} (Spin up)	5.00	4.78
Ni^{+2} (Spin down)	3.67	3.38
Ni^{+3} (Spin up)	4.72	4.49
Ni^{+3} (Spin down)	3.57	3.70
Co^{+3} (Spin up)	3.63	3.59
Co^{+3} (Spin down)	3.64	3.60
Mn^{+4} (Spin up)	4.00	3.76
Mn^{+4} (Spin down)	0.78	1.10

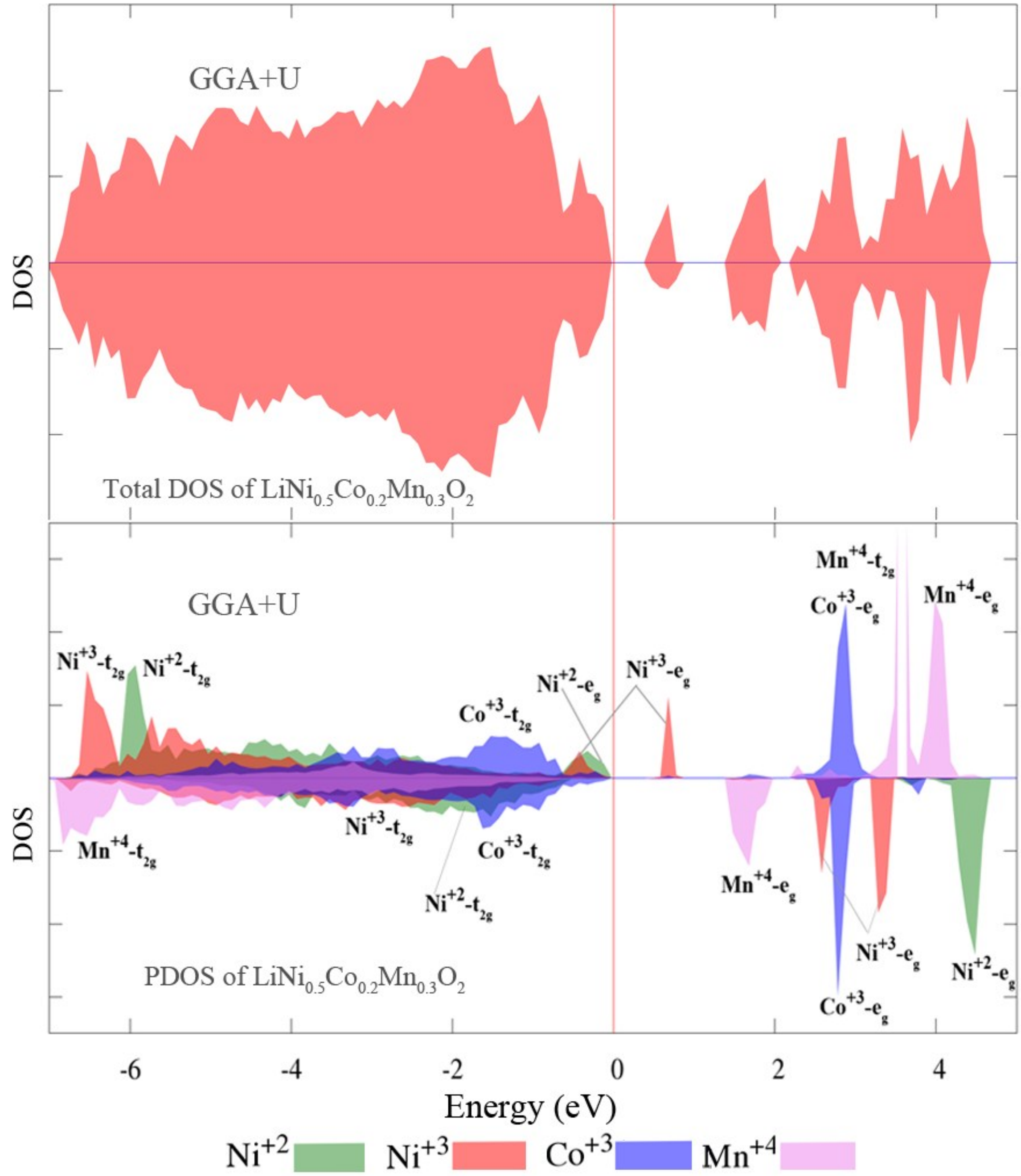

Figure S1. Density of states for $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ using GGA+U (a) total DOS (b) projected DOS.

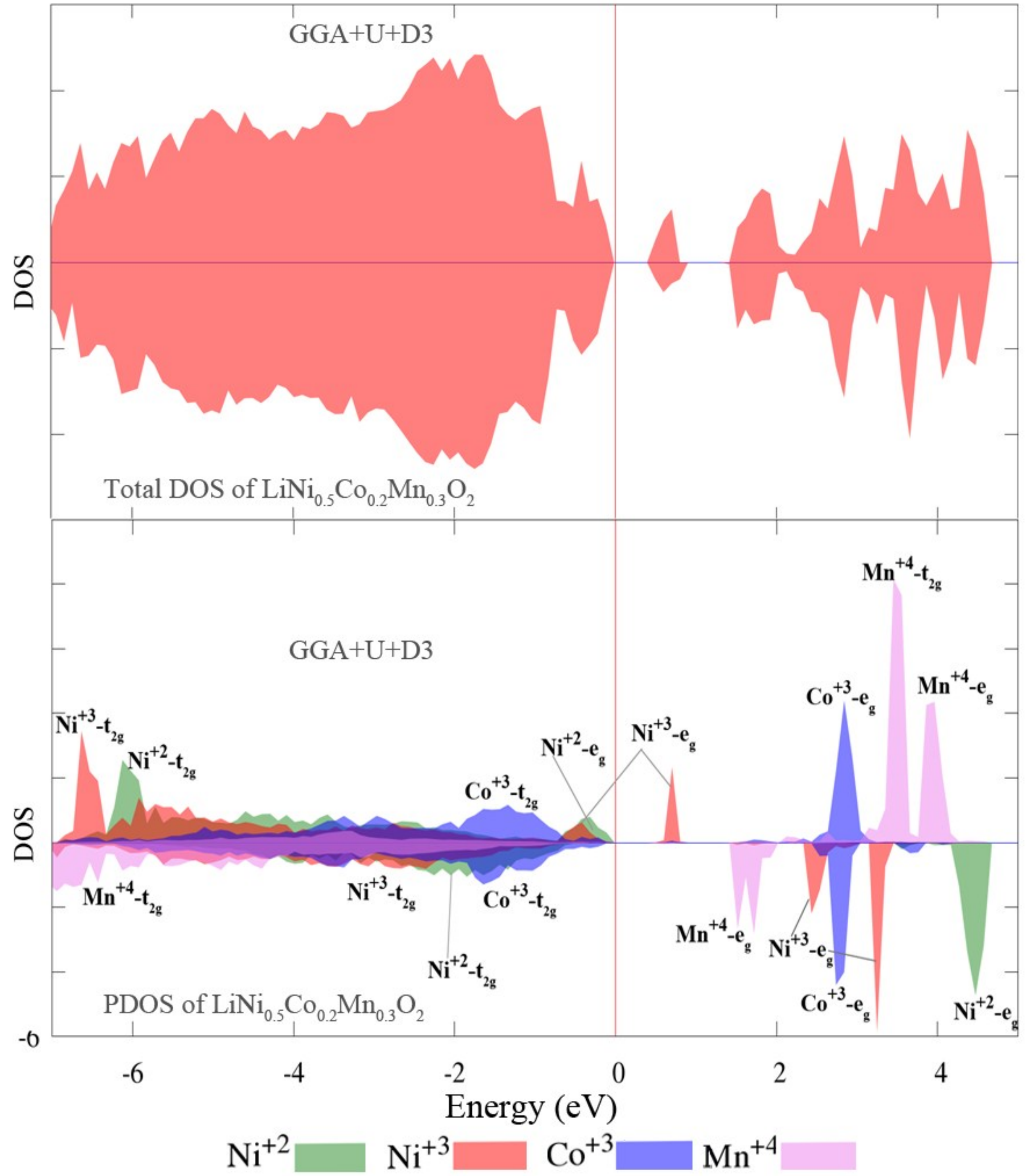

Figure S2. Density of states for $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ using GGA+U+D3 (a) total DOS (b) projected DOS.

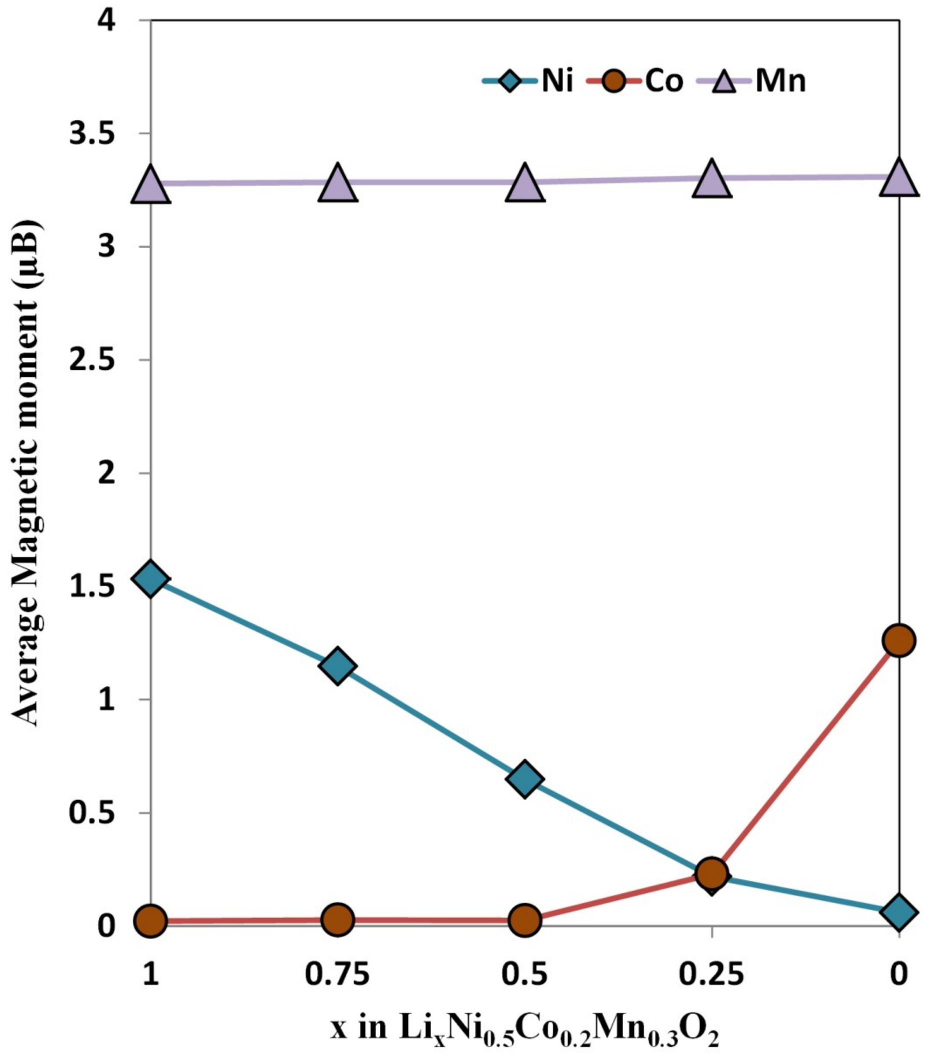

Figure S3. Change in average magnetic moments (using GGA+U) $Li_xNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ on Li de-intercalation.

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