Supporting Information

Effect of Cobalt Content on the Electrochemical Properties and Structural Stability of NCA Type Cathode Materials

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Section I. Initial structure preparation for the NCA materials:

We were dealing with a supercell with 96 (with 24 transition metal atoms) atoms and for each system, we had to consider at least 7 different structures with different Li concentration. We had to perform GGA+U which is also computationally very expensive. We were unable to consider different distribution for Li atoms due to our limited computational resources. Therefore, we have considered to remove the Li atoms randomly from the initial structure (fully lithiated). We want to mention that we have maintained the consistency while removing the Li atom. For example, if we have started with $Li_{24}Ni_xCo_yAlO_{48}$, we have generated $Li_{20}Ni_xCo_yAlO_{48}$ by removing 4 Li atoms from the same $Li_{24}Ni_xCo_yAlO_{48}$. Then again, $Li_{16}Ni_xCo_yAlO_{48}$ was generated from the $Li_{20}Ni_xCo_yAlO_{48}$ from the previous step and so on. In this way, for a particular system ($Li_{24}Ni_xCo_yAlO_{48}$), the arrangement of Li and their removal was consistent and stepwise as the delithiated structure from the previous step was used to generate a particular structure.

On the other hand, the arrangements of Co and Al atoms were tested via considering around 10 different combinations and the system with the lowest energy was chosen for further studies. In this regard, we want to clarify that we have started with the LNO structure ($Li_{24}Ni_{24}O_{48}$) and then 10 different random combinations of 4 Co atoms and 1 Al atom was chosen and the Ni atom was replaced by the Co and Al in order to generate NCA_I. For NCA_II/III/IV, we have randomly removed the Co atoms from the already existing NCA_I and replaced them by Ni. For each and every case, we have done the optimization via both ion and cell relaxation. Furthermore, this study aims to provide a qualitative approach in order to implement the idea of less cobalt usage in LIB. Our study will hopefully provide a starting point for a more detailed study on the ordered versus disordered patterns[1-2] in future.

Section II. Comparison with vdW-inclusive functional:

We have implemented vdW-inclusive GGA functional (optPBE-vdW) in order to plot the intercalation potential versus capacity. In this regard, we have considered two systems NCA_I, NCA_IV for calculating their intercalation potential and plotted the same versus capacity (See **Figure S1**). From **Figures S1**(vdW-inclusive GGA) and **Figure 3**(GGA+U), it is clear that both the functionals show similar trend and respond in a similar way due to the decrease in Co content.

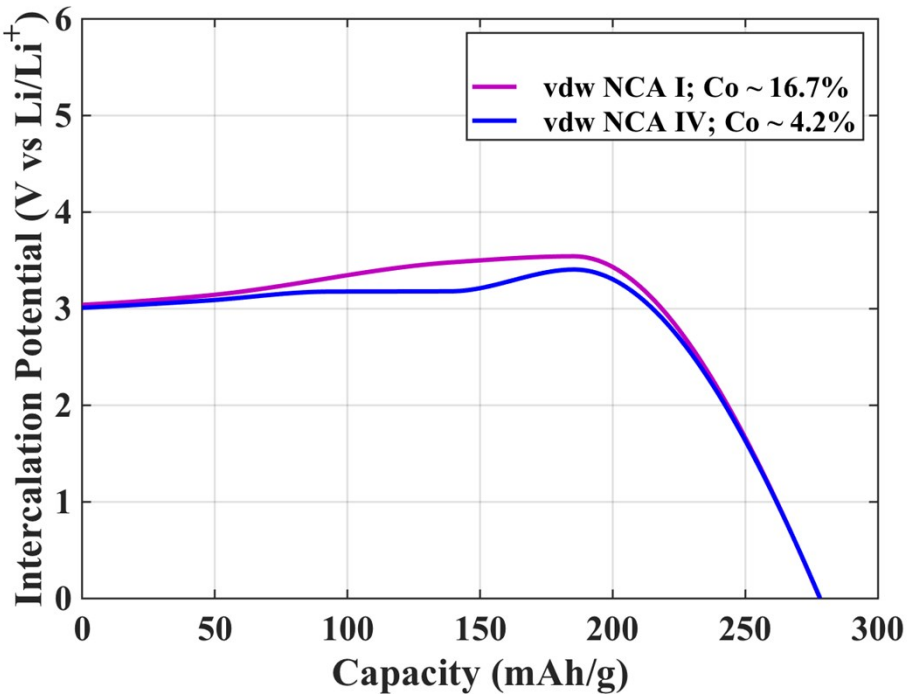

Figure S1. Comparative plot of intercalation potential (V vs. Li/Li+) with varying theoretical specific capacity for NCA_I and NCA_IV using vdW-inclusive GGA.

However, we have observed that the range of average potential value decreases for both the NCAs (3.71V – 3.23V) when using vdW-GGA as compared to the GGA+U values. In this case

NCA_I has the highest average value followed by the NCA_IV as per the prediction. An overall average potential drop of 12.9% was observed while going from NCA_I to NCA_IV which is comparable with the value computed (14.7%) using GGA+U.

Section III. Change in elastic modulus due to drop in Li and Co content

We have considered two different NCAs (NCA_I and NCA_IV) for two extreme cases of Li contents (Li_0 and Li_{24}). All the calculations were done in VASP following the method used by Maxisch and Cedar group using GGA+U functional.[3] Since, polycrystalline electrodes are isotropic, they have been modelled as isotropic elastic system. C_{ij} matrix elements obtained from VASP for triclinic system was used to calculate bulk modulus and shear modulus using Reuss-Hill schemes for triclinic system.[4] In this present study, our first observation is that both the NCAs (NCA_I and NCA_IV) don't exhibit significant change in the values of Young's modulus (E) upon delithiation. Our calculated E values for NCA_I range from 107.80 Gpa (Li_{24}) to 73.78 Gpa (Li_0). However, this range is different for NCA_IV and varies from 128.76 Gpa (Li_{24}) to 89.25 Gpa (Li_0). Though the individual E values differ for both the NCAs, the drop in E values due to delithiation for both the cases directs towards the elastic softening. The extent of softening is almost similar and are about ~31% for NCA_I and ~30% for NCA_IV.

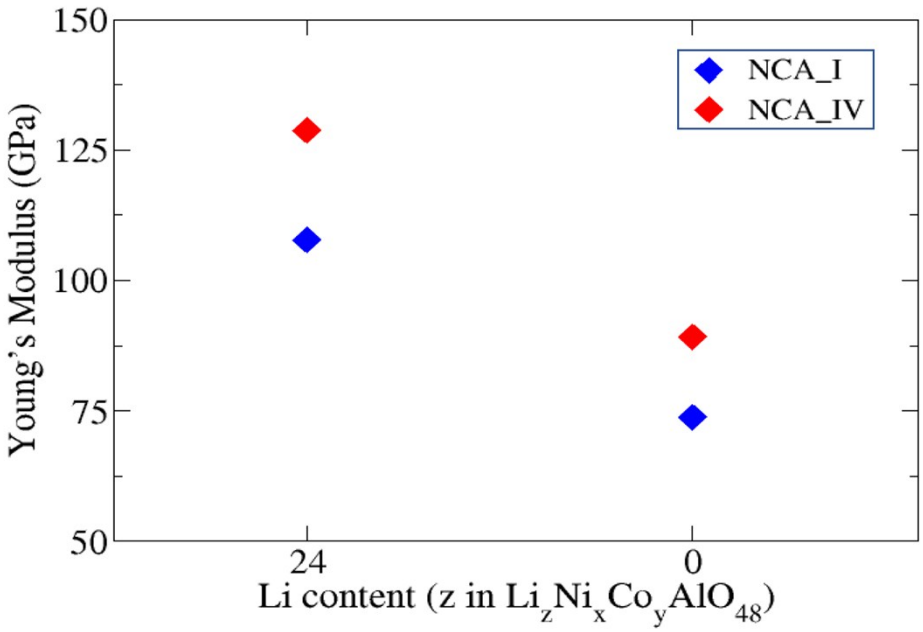

Figure S2: Comparative trend of variation of Young's modulus (E in GPa) with different Lithium content for NCA_I and NCA_IV materials.

It is important to mention here that similar behavior upon delithiation was reported for $LiCoO_2$ cathode material.[5] This behavior is quite expected since Li donates charge and cause strong ionic interlayer interactions between the layered oxides and therefore responsible for the strength of the Lithiated structure. Removal of Li causes change of ionic interactions to weak van der Waals interaction in between the oxide layers resulting in elastic softening. In either of the structure, Poisson's ratio didn't show any change upon changing Li concentration. Most importantly, we

note that NCA_IV_Li_{24} has higher E than NCA_I_Li_{24} (as shown in **Figure S2**) which points to the fact that reduction of cobalt content hardens the material. Such hardening is beneficial in matter to avoid surface cracking during repeated delithiation and lithiation.

Section IV. Cost-effectiveness with reduced cobalt concentration

We can estimate the overall cost effectiveness as follow:

Cobalt cost/lb (15th March, 2018)[6] = 39.58 USD

Nickel cost/lb (15th March, 2018)[7] = 6.21 USD

Cost reduction due to decrease in cobalt concentration = 29.68 USD/lb

Cost increment due to increase in nickel concentration = 0.98 USD/lb

The overall cost saving = 28.7 USD/lb

Most importantly, the cost of Cobalt increased in significant extent during the last year itself. The increment between January 2017 (14.2 USD/lb) and March 2018 (39.58 USD/lb) is ~25.38 USD/lb. An overall 75% reduction of Co concentration will not only lead to huge cost saving for the battery production, but it also implements an additional environmental benefit due to the reduction of overall toxicity. Moreover, NCA_IV and Na_NCA_IV, containing mostly Ni, are perfect agents for economical usage due to the cheaper cost and higher capacity of Ni as compared to the Co.[8-10].

Table S1. Comparison of structural parameters (interatomic distances) of **NCA_I** and **NCA_IV** for fully lithiated, 50% lithiated and completely delithiated states.

System	avg. bond dist. (Ni-O) in Å	avg. bond dist. (Co-O) in Å	avg. bond dist. (Al-O) in Å	avg. intra layer bond dist. (Ni-Ni) in Å	avg. inter layer dist. (Ni-Ni) in Å
NCA_I_Li_{24}	2.003	1.931	1.932	2.879	5.053
NCA_I_Li_{12}	1.912	1.903	1.925	2.835	5.153
NCA_I_Li_0	1.866	1.882	1.899	2.831	5.228
NCA_IV_Li_{24}	1.948	2.001	1.942	2.867	5.039
NCA_IV_Li_{12}	1.894	1.984	1.924	2.834	5.155
NCA_IV_Li_0	1.856	1.874	1.896	2.780	5.216

Table S2. Comparison of structural parameters (interatomic distances) of **Na_NCA_I** and **Na_NCA_IV** for fully lithiated, 50% lithiated and completely delithiated states.

System	avg. bond dist. (Ni-O) in Å	avg. bond dist. (Co-O) in Å	avg. bond dist. (Al-O) in Å	avg. intra layer bond dist. (Ni-Ni) in Å	avg. inter layer dist. (Ni-Ni) in Å
Na_NCA_I_Li_{22}	1.970	1.887	1.948	2.887	5.109
Na_NCA_I_Li_{10}	1.898	1.881	1.937	2.867	5.231
Na_NCA_I_Li_{0}	1.894	1.873	1.917	2.871	5.610
Na_NCA_IV_Li_{22}	1.975	1.944	1.942	2.898	5.113
Na_NCA_IV_Li_{10}	1.906	1.892	1.931	2.824	5.347
Na_NCA_IV_Li_{0}	1.886	1.885	1.910	2.787	5.893

Table S3. Cell volume change of NCA_Is, NCA_IVs during the lithiation/delithiation process.

System	Volume $Å^3$
NCA_I_LI0	822.124
NCA_I_LI12	816.688
NCA_I_LI24	819.508
NCA_IV_LI0	795.612
NCA_IV_LI12	815.183
NCA_IV_LI24	818.368
Na_NCA_I_LI0	876.721
Na_NCA_I_LI10	837.450
Na_NCA_I_LI22	837.058
Na_NCA_IV_LI0	880.819
Na_NCA_IV_LI10	836.747
Na_NCA_IV_LI22	830.356

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