

First principles investigation into the interwoven nature of voltage and mechanical properties of the $\text{Li}_x\text{NMC-811}$ cathode

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Abstract

Density functional theory has been used to investigate the electrochemical and mechanical properties of the well-known cathode material $\text{Li}_x\text{Ni}_{0.833}\text{Mn}_{0.083}\text{Co}_{0.083}\text{O}_2$ ($\text{Li}_x\text{-NMC-811}$) as a function of Li concentration. We used the PBE functional with dispersion corrections to calculate a voltage in good agreement with experiment, which gradually changes from 3.3 to 4.2 V during the charging process. A similar profile trend can be found without dispersion, though voltages were lower by ~ 0.4 V and the known NMC lattice collapse was not captured as it was with dispersion. We compare calculated quantities such as Young's modulus (E) to better understand the mechanical response of the material to outside forces with varying Li concentration. We also compare Poisson's ratio (ν) and the Pugh ratio (γ), which are used as metrics of ductility, for each of these lithiation concentrations. We have shown that as the concentration of Li reaches $x = 0.25$, the material transitions from ductile to brittle based on both ductility metrics. It is near this concentration that we also see the largest change in voltage from our calculations. We propose that this transition between ductile and brittle provides additional insight and understanding to structural failure and, consequently, capacity loss during normal cycling for cathode materials. Furthermore, it demonstrates a mechanism for reversibly controlling mechanical properties by electrochemical means.

Keywords: Density functional theory, NMC, energy storage, mechanical properties, ductility

1. Introduction

Since its development in the latter half of the 20th century, the Li ion battery (LIB) has revolutionized nearly every aspect of our daily lives [1, 2]. Its high energy density and specific capacity has led to its use in many modern electronic devices. However, there has been a recent

demand for improved performance, lower cost, better stability, and lower environmental impact [3, 4, 5, 6], which has led to the use of materials design to optimize the performance of current battery cathodes [7, 3, 8, 9, 10]. Although various transition metal oxides have been investigated [11, 12, 13], the tunable nature of $\text{Ni}_a\text{Mn}_b\text{Co}_c\text{O}_2$ (where $a + b + c = 1$), has made it a front runner for

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use in LIBs [9, 14].

Throughout various investigations, $\text{Ni}_a\text{Mn}_b\text{Co}_c\text{O}_2$ (NMC-*abc*) compounds have been shown to possess desirable characteristics such as high specific capacities and the ability to achieve high voltages. Although having shown the capability to reach well over 4 V, NMC cathodes are typically unable to compete with the industry standard of $\sim 300 \text{ mAh g}^{-1}$ for specific capacity in LIBs [9, 14, 15, 16, 17]. Despite their promising electrochemical performance and extensive use within industry, several reported issues have plagued NMC compounds. In particular, mechanical failure as a result of changes to the structure that regularly occurs during cycling [15, 18, 19, 20]. As the structure moves towards failure, cavitation and fracturing contribute to a degradation in the quality of the material [14, 18]. This less stable structure results in a decreased capacity for the cathode, as well as altering the overall integrity of the entire battery which weakens conduction, reduces efficiency, and is known to cause catastrophic failure of batteries [21, 22, 23, 24, 25, 14]. Previous works have investigated the effects of stress accumulation within battery interfaces [26, 27], where failures will occur at the brittle interfaces because of the inability to accommodate the stress introduced to the system during charge/discharge cycling [28]. Due to these failures, it has become a necessary part of battery research to thoroughly explore the mechanical properties of all components [29].

Despite increased difficulty in performing mechanically

driven experiments on NMC materials due to their reactive nature with air [30], there are various concentrations of NMC of which the mechanical properties have been investigated to some extent (*e.g.*, NMC-333, NMC-442, NMC-532, NMC-622, and NMC-811) with a mixture of experimental and computational results [16, 17, 9, 14]. Throughout these works there is significant investigation of the Young’s modulus and hardness of these various NMC materials [17, 9, 14], with additional investigations into Poisson’s ratio [17], the coefficient of thermal expansion [9], and interfacial fracture toughness [14]. Additional thermal quantities (including Helmholtz free energy, vibrational entropy, and specific heat) have also been studied to some extent [9]. Most notably, this collection of previous work indicates that each of these structural properties (Young’s modulus, hardness and overall mechanical strength) will decrease overall as the battery is continually cycled [16, 17, 9, 14]. There is a significant amount of data for NMC-*abc* compounds, however, there is a lack in consistency in reporting of particular properties of interest, which makes it very challenging to draw any conclusions on the overall mechanical properties of these battery materials. It would be of great benefit to focus research efforts into developing a database of such properties.

In this work, we use first-principles density functional theory (DFT) calculations to investigate the electrochemical and mechanical properties of $\text{Li}_x\text{Ni}_{0.833}\text{Mn}_{0.083}\text{Co}_{0.083}\text{O}_2$ (hereafter referred to as NMC-811) as a function of Li concentration. Calculation

of the bulk (K) and shear (G) moduli provide us with enough information to compute Young’s (E) modulus, as well as Poisson’s ratio (ν) and the Pugh ratio (γ), which we use to investigate changes in ductility through various intercalation concentrations. We are then able to compare these mechanical quantities to the calculated voltage profile of $\text{Li}_x\text{NMC-811}$ to further investigate the implications of changes in such properties.

2. Computational methods

2.1. Computational details

DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [31, 32, 33, 34, 35, 36]. VASP uses a plane wave basis set, and ion-electron interactions were approximated using the projector augmented wave (PAW) potentials [37]. Both the kinetic energy cutoff and k -point grid were tested with the criterion for convergence being an energy variation of less than 1 meV/atom. A plane wave energy cutoff of 700 eV and a Γ -centered $3\times 3\times 1$ Monkhorst-Pack [38] k -point grid were found to be sufficient for all calculations. The Brillouin zone was sampled by the use of Gaussian smearing and all structural relaxations and energy calculations were performed using the Perdew-Burke-Ernzerhof (PBE) functional [39], both with and without the inclusion of van der Waals (vdW) interactions by means of the zero-damping method (DFT-D3) of Grimme [40].

2.2. Relaxations

A full structural relaxation, including lattice vectors, was performed on the fully lithiated (*i.e.*,

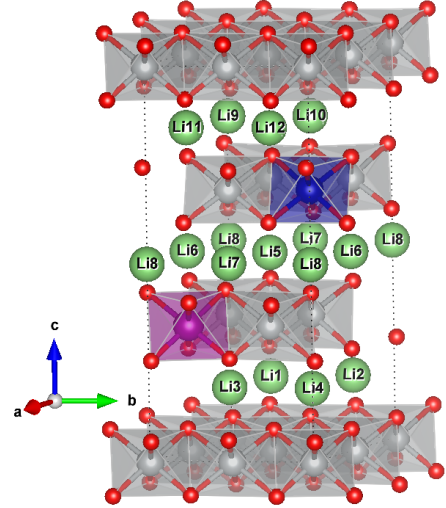


Figure 1: The Li-NMC-811 cell shown in color with Li (green), O, (red), Ni (gray), Co (blue) and Mn (purple), with each intercalation site labeled. Crystallographic information for this structure can be found in Table S1 in the Supplemental Material [41].

$\text{Li}_1\text{Ni}_{0.833}\text{Mn}_{0.083}\text{Co}_{0.083}\text{O}_2$, or Li-NMC-811), material. The initial atomic configuration (where the supercell, modeled after Ref. [42], is in the $R\bar{3}m$ space group) is provide in Table S1 [41]. Deintercalation of Li (*i.e.*, charging) was simulated by a sequence of configuration comparisons (*i.e.*, site testing). For example, the structure of one Li atom being removed from Fig. 1 ($x = 0.917$) was determined by comparing the energy of all possible configurations resulting from a single Li atom being removed from the 12 octahedral sites within our simulation cell. Then, the lowest energy configuration was kept as the final structure for this Li concentration. This structure was then used to determine the lowest energy configuration for $x = 0.833$ by comparing the energies of individually removing each of the remaining 11 Li atoms. This process was repeated until the cathode was completely void of Li, with each of the most energetically favorable structures being used in all ensuing calculations. This procedure

yielded the following as the most energetically favorable sequence for removing Li atoms: 4, 7, 12, 1, 6, 10, 8, 3, 11, 2, 9, 5 for PBE and 11, 5, 3, 8, 10, 4, 7, 12, 1, 2, 9, 6 for PBE-D3, with the numbers corresponding to the labels in Fig. 1. Because we are using a relatively small cell to simulate our system, we are limited in the possible number of Li concentrations which can be investigated. A more detailed landscape would provide more insight into the overall mechanical nature of the NMC-811 cathode; however, the current work provides the groundwork for further exploration into alternate Li concentrations.

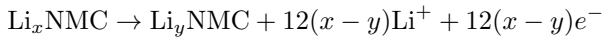
Upon completion of the site testing, formation energies were computed for all Li concentrations. Formation energy, E_{Form} , was computed using

$$E_{\text{Form}} = E_{\text{Li}_x\text{NMC}} - xE_{\text{Li-NMC}} - (1-x)E_{\text{NMC}}. \quad (1)$$

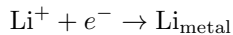
In the above equation, $E_{\text{Li}_x\text{NMC}}$ is the energy of the partially intercalated NMC-811 cathode, $E_{\text{Li-NMC}}$ is the energy of the fully intercalated cathode (as shown in Fig. 1), and E_{NMC} is the energy of the fully delithiated NMC-811 structure. After E_{Form} was determined, a convex hull was created (see Fig. S1 [41]) to determine the stability of each Li concentration structure.

2.3. Voltage

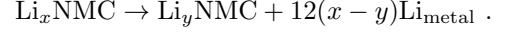
To compute voltages for our simulated charging process, we focus on the half-reactions



and



for the cathode and anode, respectively, where x and y are Li concentrations such that $x > y$. It should be noted that the “12” in the cathode half-reaction is due to the supercell used (*i.e.*, 12 total Li ions). The combination of these half-reactions yields the overall reaction of



This overall reaction corresponds to $12(x-y)$ electrons being transferred from the cathode to the anode when delithiating $12(x-y)$ Li atoms from NMC-811. It then follows that voltage can be calculated as

$$V = \frac{(E_{\text{Li}_y\text{NMC}} + 12(x-y)E_{\text{Li}_{\text{metal}}}) - E_{\text{Li}_x\text{NMC}}}{12(x-y)}, \quad (2)$$

where $E_{\text{Li}_y\text{NMC}}$ and $E_{\text{Li}_x\text{NMC}}$ are the energies of Li_yNMC -811 and Li_xNMC -811, respectively, and $E_{\text{Li}_{\text{metal}}}$ is the energy per atom of a pure Li metal anode. This process was utilized only for those intercalation concentrations residing on the convex hull in Fig. S1 [41] to create the final voltage profile shown in Fig. 3.

The calculation of voltage in this manner is an approximation since volume and entropy effects are neglected and only the internal energy of each system is considered. Inclusion of volume and entropy effects has been shown to contribute less than 0.2 V while greatly increasing computational cost [43, 44, 45, 46, 47, 48]. In addition, all surface interactions have been neglected in this work as it is assumed that ions can readily intercalate within the bulk of NMC-811 based on previous experimental works [49, 50, 51, 52, 53, 54, 55, 56, 57, 58].

2.4. Elastic properties

In previous work [59, 60, 29], we have shown that the elements of the elastic tensor (C_{ij}) can be calculated using the generalized stress-strain variant of Hooke's Law,

$$\sigma_i = C_{ij}\epsilon_j, \quad (3)$$

where σ_i and ϵ_j are the stress and strain, respectively. This requires that after completing the structural relaxation, we apply an artificial strain along one dimension ($\pm 0.5\%$ and $\pm 1.0\%$) and two dimensions ($\pm 3.0\%$ and $\pm 6.0\%$). The internal stress of the system is calculated along each possible axis of applied strain in individual simulations. This tensor provides us with sufficient information to calculate the bulk modulus (K) and the shear modulus (G) for a given material (calculated values are provided in Table S4 of the Supplemental Material [41]). We use the Voigt-Reuss-Hill (VRH) approximation to extract polycrystalline properties from single crystal data [61]. We use the following equations to obtain the upper bound of K and G ,

$$K_V = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{23} + C_{13}), \quad (4)$$

$$G_V = \frac{1}{15}(C_{11} + C_{22} + C_{33}) - \frac{1}{15}(C_{12} + C_{23} + C_{13}) + \frac{1}{5}(C_{44} + C_{55} + C_{66}). \quad (5)$$

To obtain the Reuss variants of K and G (*i.e.*, the lower bound), we use the inverse of the elastic tensor (the compliance tensor), where S_{ij} are the matrix elements of the compliance tensor, allowing us to calculate K_R and G_R ,

$$\frac{1}{K_R} = (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{13}), \quad (6)$$

$$\frac{1}{G_R} = \frac{4}{15}(S_{11} + S_{22} + S_{33}) - \frac{4}{15}(S_{12} + S_{23} + S_{13}) + \frac{1}{5}(S_{44} + S_{55} + S_{66}). \quad (7)$$

The (VRH) averages for K and G can be calculated as

$$K = \sqrt{K_V K_R}, \quad (8)$$

$$G = \sqrt{G_V G_R}. \quad (9)$$

With the calculated quantities K and G , we are able to compute additional physical properties such as Young's modulus (E), Poisson's ratio (ν), and the Pugh ratio (γ),

$$E = \frac{9KG}{3K + G}, \quad (10)$$

$$\nu = \frac{3K - 2G}{2(3K + G)}, \quad (11)$$

$$\gamma = \frac{K}{G}. \quad (12)$$

We have used both Poisson's ratio and the Pugh ratio in previous work as calculated metrics of ductility [59, 60, 29]. Since these particular quantities are determined from K and G , they offer a straightforward method of predicting ductility from first principles. As a general guide, a material with a Pugh ratio greater than 1.75 is ductile, whereas one with a Pugh ratio less than 1.75 is brittle [62]. This is a common technique used for assigning ductility to a material even though Pugh's original works were related to phenomenological findings [62]. Similarly, Poisson's ratio is another dimensionless quantity that is used as a metric for ductility. A Poisson's ratio greater than 0.26 indicates ductility, while a Poisson's ratio less than 0.26 denotes brittleness. This technique is typically applied to other materials (alloys, etc.), but we expect it to be insightful

for cathode analysis. The question of its reliability is of great interest, though we expect dramatic changes in the Poisson's and Pugh ratios to reflect changes in ductility, even if the exact boundary value is different from that typically used in other materials.

3. Results and discussion

3.1. Structure and Site Testing

With and without the inclusion of dispersion effects, the resulting structural relaxations maintained the $R\bar{3}m$ crystal structure for the fully lithiated and delithiated structures as shown in Fig. 1. The resulting averaged a, b -lattice vector, c -lattice vector, and cell volume are shown in Fig. 2, as a function of Li concentration with comparison between various other computational [42, 63, 64] and experimental works [49, 50, 51, 52, 53] (numerical values of all lattice parameters are shown in Tables S2 and S3 for PBE and PBE-D3, respectively [41]). Throughout delithiation, the a, b -lattice vector undergoes a general trend of contracting. From fully lithiated to fully delithiated, the vector only undergoes a 2.0% and 1.3% decrease for PBE and PBE-D3, respectively. As shown in Fig. 2a, both PBE and PBE-D3 are in good agreement with other works, while PBE-D3 has better overall agreement with experimental works [49, 50, 51, 52, 53].

With the c -lattice vector (Fig. 2b), we find a general expansion from fully lithiated to $x = 0.25$ in $\text{Li}_x\text{NMC-811}$ for PBE. After this concentration, PBE undergoes a slight contraction at $x = 0.083$. With PBE-D3, the structure

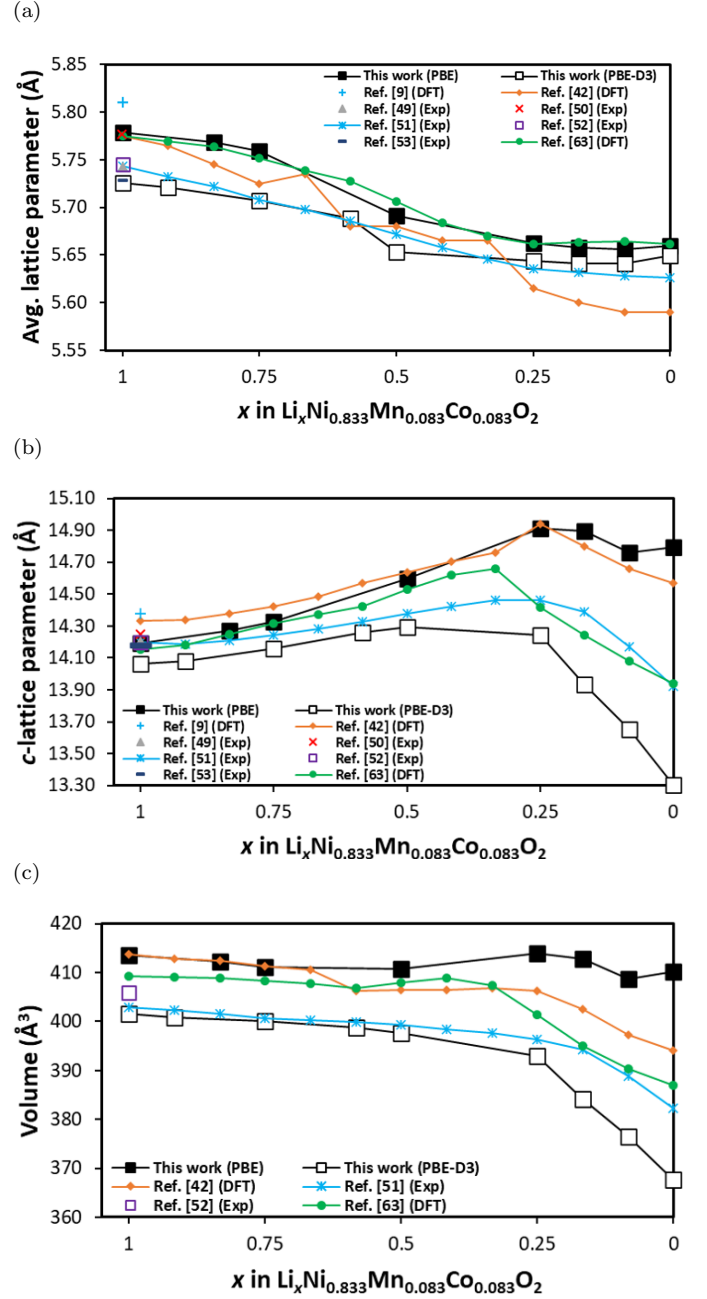


Figure 2: Resulting (a) a, b -lattice vector average, (b) c -lattice vector, and (c) cell volume during the delithiation process for this work and others [9, 42, 63, 49, 50, 51, 52, 53].

initially expands until $x = 0.5$. Following this, the material undergoes a lattice collapse from $x = 0.25$ to full delithiation, in agreement with previous works [51, 63]. With the behavior of lattice vectors a, b and c , the volume (Fig. 2c) for PBE remains fairly unchanged (changing

by only 0.81%) during the delithiation process. However, when we include dispersion, the collapse of the c -lattice vector causes a larger decrease in volume (8.44%).

The results of the relative formation energy calculations using PBE and PBE-D3 are shown in Fig. S1, with the numerical results of the calculations also provided in Tables S2 and S3 [41]. For all mechanical properties calculations, each concentration was investigated but only values which lie on the hull are shown in this work, while all other values are provided in Table S4 [41].

3.2. Voltage

Using the results shown in Fig. S1 [41] and Eqn. 2, voltages were calculated for each stable $\text{Li}_x\text{NMC-811}$ system and are presented in Fig. 3. Voltages are only calculated for concentrations which lie on the convex hull as they are the only ones expected to be thermodynamically stable. We note that lithium is unlikely to be entirely extracted in the experiment, but we are interested in determining how the properties change throughout the delithiation process, leading to calculations of the mechanical properties at multiple concentrations from $x = 1$ to $x = 0$. While some of the values we calculate may not be achieved experimentally, they offer valuable insights into how the cathode properties change in extreme conditions. When dispersion effects are included, the largest change in our calculated voltages occur when charging from $x = 0.25$ to $x = 0.167$. Without dispersion, the largest change occurs from $x = 0.167$ to $x = 0.083$. Further discussion on these changes can be found in Sec. 4.

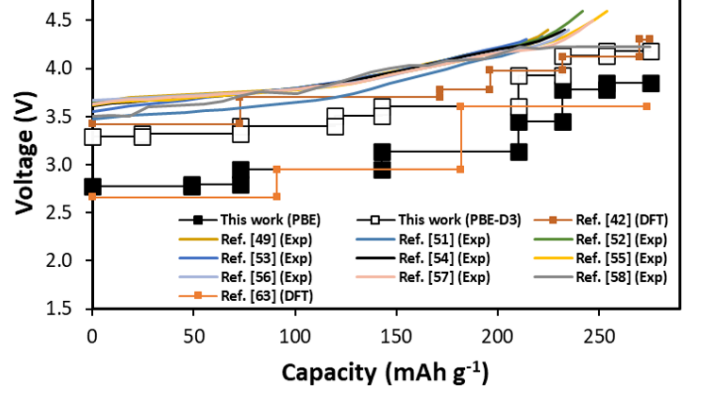


Figure 3: Calculated voltage for each stable $\text{Li}_x\text{NMC-811}$ system using PBE and PBE-D3 (filled and empty black squares, respectively). Other DFT (small squares) and experimental (curved lines) works are included as well.

Results from experimental [49, 51, 52, 53, 54, 55, 56, 57, 58] and computational [42, 63] investigations are also reported on Fig. 3 for comparison. It can be seen that standard DFT (PBE) underestimates the voltage when compared to experiment, whereas the inclusion of dispersion effects (PBE-D3) yields voltages in better agreement with previously reported values. Due to the agreement between our calculated values and reported experimental values for the structural and electrochemical properties, we believe that a sufficient level of theory has been reached with PBE-D3.

3.3. Mechanical Properties

3.3.1. Elastic Moduli

The resulting calculations for the bulk (K), shear (G) and Young's (E) moduli are shown in Fig. 4a, with numerical values for all calculated properties with PBE and PBE-D3 provided in Table S4 [41]. For concentrations of $x \geq 0.5$, each of the elastic moduli are almost unchanged (for changes in concentration, and across functionals). For $x \leq 0.25$ the values diverge when comparing the calcula-

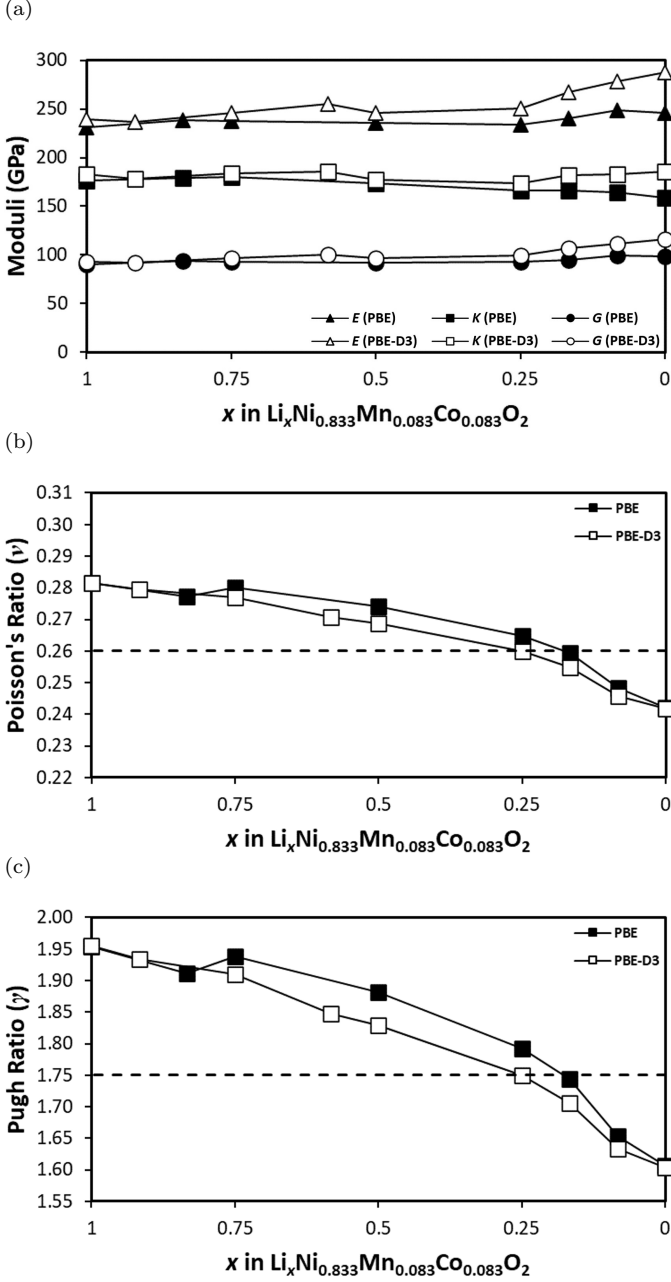


Figure 4: (a) Elastic moduli, (b) Poisson's Ratio, and (c) Pugh ratio of $\text{Li}_x\text{NMC-811}$ as a function of Li concentration.

tions with and without dispersion. G shows an increase in magnitude for both functionals, however the inclusion of dispersion shows a greater increase as concentration decreases. For K , PBE shows a decrease until empty ($x = 0$); however, dispersion effects cause a slight increase in K from $x = 0.25$ to $x = 0$. Because E is calculated from

both K and G , the divergence in the functionals is more exaggerated. Here, we see an increase with and without dispersion, but dispersion shows a more significant increase as we continue removing Li.

3.3.2. Ductility metrics

Both Poisson's ratio (ν) and the Pugh ratio (γ) (shown in Fig. 4b and 4c, respectively) show identical trends as a function of Li concentration in $\text{Li}_x\text{NMC-811}$. The fully lithiated cathode is predicted as (noticeably) ductile with both PBE and PBE-D3. From there, we show a continuous decrease in ductility throughout all Li concentrations when using PBE-D3, transitioning from ductile to brittle near $x = 0.25$. For PBE, however, there is a slight increase in ν and γ at $x = 0.75$, with continual decreasing values thereafter. Here, the transition between ductile and brittle occurs around $x = 0.167$.

For concentrations of Li between 0.167 and 0.75, if we compare the two functionals, both metrics of ductility appear to diverge before converging at both ends ($x = 0$ and $x = 1$). The most significant difference for the two functionals occurs at $x = 0.5$ for both ν and γ . For this specific point, we believe this difference comes from the (largest) decrease in the a, b -lattice vector when we include dispersion ($0.12 \text{ \AA}$). Furthermore, in the region where $x < 0.25$ the metrics for ductility shift downwards such that the location at which the functionals cross the ductile/brittle boundary is different. However, the fully delithiated structure again shows no difference in the ductility metrics between the two functionals.

For further analysis of the electronic properties, we have included the PDOS results calculated with PBE and PBE-D3 in Fig. S2 and S3, respectively, where we see the general trend of depopulation of O(p) states through delithiation across the ductile/brittle boundary. For additional insight into structural changes, we have provided the radial distribution function for various atomic combinations calculated with PBE and PBE-D3 in Fig. S4 and S5, respectively, where one can see minimal structural changes occur through delithiation across the ductile/brittle boundary [41].

4. Discussion

The overall consistent volume in $\text{Li}_x\text{NMC-811}$ when calculated with PBE throughout the charging process would indicate that we would not expect a significant decrease in capacity due to strain through cycling. However, capacity loss is a known issue [54] and as such requires the need for further examination. The experimentally measured collapse of the c -lattice vector required us to further investigate the material properties using PBE-D3 (*i.e.*, including dispersion). Overall, PBE-D3 provides better agreement with experimental findings for the structural and electrochemical properties of $\text{Li}_x\text{NMC-811}$. Even so, the calculation of the mechanical properties of $\text{Li}_x\text{NMC-811}$ using both functionals has provided insight into the correlation between large changes in voltage and the ductile/brittle transition in this particular cathode.

The overall mechanical properties of this system are

changing such that once delithiation occurs to a level below $x = 0.25$, a drastic transition in functionality occurs. For PBE-D3, the point at which the cathode crosses the ductile/brittle boundary not only corresponds to the largest change in the voltage profile, but it also coincides with the beginning of the experimentally proven lattice collapse. Thus, as the cathode passes this ductile/brittle boundary throughout the cycling process, the NMC-811 material is increasingly less capable of withstanding the additional stress that is associated with the deintercalation of Li ions; potentially explaining the corresponding lattice collapse, leading to a decreased ability to accommodate those ions (capacity), as well as cracking over time.

It has been shown experimentally that layered oxides commonly experience capacity loss after their first cycle, and it has been determined that if a cathode of this nature were to reach a completely delithiated state, that the maximum theoretical capacity cannot be retained [54]. Throughout the process of charge cycling, $\text{Li}_x\text{NMC-811}$ will regularly cross the ductile/brittle boundary based on the degree to which it is charged. We believe that over time the repeated transition across the ductile/brittle boundary (as well as other changing mechanical properties) will be a key component in the overall lifetime performance of $\text{Li}_x\text{NMC-811}$ as a battery cathode.

5. Summary and conclusions

By investigating the ductility of $\text{Li}_x\text{NMC-811}$, we have shown that the mechanical and electrochemical properties

are interwoven such that changes in either property corresponds to a significant change in the other. In particular, we have shown that the transition from ductile to brittle (as determined by both Poisson’s ratio and the Pugh ratio) corresponds to the most significant change in voltage for $\text{Li}_x\text{NMC-811}$ when using both PBE and PBE-D3 without significant corresponding changes in the electronic and/or physical structures. For the supercell that we have studied in this work, it is also below this concentration ($x = 0.25$) that the layered material will begin to completely empty layers of Li. Since the material is now brittle, it is our conjecture that during further delithiation that the battery will not be able to withstand this stress and the cathode will experience a significant decrease in capacity, while also facing a significant possibility of cracking due to significant collapse of its lattice. While most fractures of the cathode occur along grain boundaries or other material interfaces [65], the overall embrittlement of the bulk will contribute to the degradation of the entire material due to an inability to accommodate the repeated stress of charge cycling. It is our hope that this work inspires future investigations to further the understanding of the connection between a cathodes ductility and its structural and electrochemical performance. This phenomenon may open the door towards state-of-the-art materials whose mechanical properties can be reversibly controlled by electrochemical means.

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- [41] See Supplemental Material at [URL will be inserted by publisher] for Table S1 which provides crystallographic information for the structure used in this work. Figure S1 shows the convex hull calculated for PBE and PBE-D3. Figures S2 and S3 show the PDOS for PBE and PBE-D3, respectively. Figures S4 and S5 show the radial distribution function for multiple atomic combinations at different concentrations for PBE and PBE-D3, respectively. Table S2 - S3 which provide the relaxed lattice parameters, formation energy, and voltages for each concentration of Li using PBE and PBE-D3, respectively. And Table S4 which contains the numerical values of the mechanical properties for PBE and PBE-D3.
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