Temperature-Dependent Dynamic Disproportionation in LiNiO$_2$

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Abstract

The layered oxide LiNiO$_2$ is the model system for high-performance Ni-rich cathodes for lithium-ion batteries. Here we investigate computationally the local electronic and spin structure and dynamics of nickels in LiNiO$_2$. Ab initio molecular dynamics simulations suggest that disproportionation of spin-half ($S = \frac{1}{2}$) nickels to $S = 0$ and $S = 1$ is favored towards cryogenic temperatures. Upon heating, the spin states of the nickels interconvert between 0, $\frac{1}{2}$, and 1 on a sub-picosecond timescale. We propose that the transitions between differing states of the Ni correspond to the heat-activated electronic conduction in LiNiO$_2$. The $S = 1$ nickels are also found to stabilize antisite nickel defects via antiferromagnetic interactions. Finally, we suggest avenues for the experimental verification of our hypothesis.

Introduction

Lithium nickel oxide, LiNiO$_2$, is the prototype material for nickel-rich layered oxides that are the leading cathode materials for automotive lithium-ion batteries [1]. For a given upper cutoff voltage, the Ni$^{3+}$ → Ni$^{4+}$ redox couple offers the highest reversible capacity of the Mn-Co-Ni series. However, the nickel chemistry is also responsible for the degradation and thermal instability of the practical cathodes at high voltage [2]. This tradeoff between capacity and stability motivates a rigorous understanding of LiNiO$_2$ as a model system.

The formally-3d$^7$ low-spin ($S=1/2$) configuration of Ni in LiNiO$_2$ is orbitally degenerate, and therefore expected to undergo a Jahn-Teller distortion. Two other mechanisms for relieving the crystal-field orbital degeneracy in the hexagonal planar lattice are via the adoption of an in-plane noncollinear arrangement of the spins [3], or via disproportionation [4,5], whereby different Ni ions adopt distinct electronic and / or geometric local environments. These alternative mechanisms are found in other layered nickelates ANiO$_2$: NaNiO$_2$ exhibits a cooperative and collinear Jahn-Teller distortion [6,7], while AgNiO$_2$ instead exhibits disproportionation, giving multiple distinct nickel environments [8,9]. A non-cooperative and dynamic Jahn-Teller effect is generally accepted for LiNiO$_2$ [10,11], although disproportionation based on Ni-O bond lengths has also been argued [12,13].

Here we investigate computationally the intersection of the disproportionation model and the dynamic Jahn-Teller model in LiNiO$_2$. The two models attempt to describe the local electronic and geometric Ni environment, respectively, and could in principle complement each other. We take a general definition of “disproportionation” as the presence of distinct nickel environments and a process of interconversion between them.
The physical properties and defect chemistry of LiNiO$_2$ have been comprehensively reviewed [10]; here we highlight a subset of experimental measurements that bears upon the local nickel chemistry and informs computations:

1. The antisite defects Ni$_{Li}$, where excess nickel takes a lithium site, are near-impossible to eliminate from LiNiO$_2$, distinguishing it from other layered oxides [10]. The concentration [Ni$_{Li}$] of the antisite defects correlates with an increased magnetization response [14–18] below room temperature.

2. LiNiO$_2$ exhibits temperature-activated p-type electronic conductivity [19], where the temperature dependence indicates either Anderson localization or a small-polaron–hopping energy that decreases upon cooling. LiNiO$_2$ with [Ni$_{Li}$] < 3% appears approximately two orders of magnitude more conductive at room temperature than NaNiO$_2$ [20], while all known polymorphs of AgNiO$_2$ are metallic [21,22].

3. Raman spectroscopy of LiNiO$_2$ shows a gradual temperature dependence, whereby additional peaks appear upon cooling [23].

4. Extended X-ray fine structure (EXAFS) measurements at the nickel K-edge are consistent with distortions of NiO$_6$ octahedra [24,25], although the studies differ in the direction of the Jahn-Teller distortions assumed for modelling the spectra, and do not take into account possible dynamics. A neutron pair distribution function (PDF) analysis [26] shows a transition between cryogenic and room-temperature structures upon heating that is gradual rather than abrupt (Figure 4 of Ref. [26]).

5. Room-temperature inverse partial fluorescence yield (IPFY) measurements with excitation at the nickel L-edge show a substantial difference between LiNiO$_2$ and NaNiO$_2$ [13], as do cryogenic-temperature neutron PDF data [26].

**Computational Methods**

We use the meta-GGA level of theory that has recently enjoyed success in representing layered lithium transition metal oxides [11,27–29]. We focus on results from simulations performed using the r$^2$SCAN functional with the revised Vydrov-van Voorhis (rVV10) non-local dispersion correction [30,31]. This combination was found to best reproduce both the thermodynamics of LiNiO$_2$ and its constituent phases [32,33], and the geometry of the delithiated layered phase NiO$_2$ (Table 1), while foregoing empirical parameters (Hubbard $U$, or fraction of exact exchange for hybrid DFT). The simulated geometries of NiO and LiNiO$_2$ are close to experimental values [6,34] and depend only weakly on the choice of functional (Table 1). We find that some of the simulated dynamics are sensitive to the choice of functional, and we present a sensitivity analysis below.

To avoid prescribing the local electronic structure as would be needed with localized basis sets, all calculations are carried out using the projector augmented-wave method [35–37] in the VASP package [38,39]. Static calculations used a 700-eV plane-wave cutoff and 0.25 Å$^{-1}$ k-point spacing, and energies and forces relaxed to $10^{-5}$ eV and $10^{-2}$ eV Å$^{-1}$, respectively, or better. For ab initio molecular dynamics (AIMD) simulations, a Γ-centered 2×2×2 k-point mesh, a 700-eV plane-wave cutoff, and a 108-atom cell were used, unless specified otherwise. AIMD simulations were carried out in the NVT ensemble with a time step of 2 fs, a Nosé-Hoover thermostat time constant of
40 steps, and electronic convergence to $10^{-4}$ eV. To identify the states of the Ni we use local spin densities, $S$, as calculated in VASP. This choice of descriptor gives a relatively unambiguous assignment for each Ni, with a high signal-to-noise resolution even in our AIMD simulations (see, e.g., Figure 2 below). Focusing on local spins avoids issues with estimating formal ionic charges to classify distinct Ni; because of the strong covalency of LiNiO$_2$ the assignment of formal charges can be sensitive to the details of the chosen charge-partitioning scheme, introducing additional difficulty in interpreting any resulting data.

Table 1: Comparison between structural and thermodynamic parameters of LiNiO$_2$ simulated with meta-GGA functionals and their experimental values.

| Parameter | SCAN | SCAN +rVV10 | r$^2$SCAN | r$^2$SCAN +rVV10 | Exp't |
|-----------|------|-------------|-----------|-----------------|-------|
| $R\bar{3}m$ a, Å | 2.85 | 2.84 | 2.85 | 2.85 | 2.878 |
| $R\bar{3}m$ c, Å | 14.10 | 14.05 | 14.10 | 14.06 | 14.19 |
| $R\bar{3}m$ $\Delta H$, eV | -6.62 | -6.74 | -6.23 | -6.35 | -6.15 |
| NiO a, Å | 4.155 | 6.146 | 4.16 | 4.15 | 4.17 |
| NiO $\Delta H$, eV | -2.73 | -2.80 | -2.41 | -2.48 | -2.48 |
| Li$_2$O $\Delta H$, eV | -6.16 | -6.21 | -6.04 | -6.09 | -6.20 |
| NiO$_2$ a, Å | 2.77 | 2.77 | 2.78 | 2.78 | 2.81 |
| NiO$_2$ c, Å | 13.67 | 13.08 | 13.63 | 13.21 | 13.3 |

In the AIMD simulations, substantial variation in spin was observed only for Ni. Spins on oxygens never exceeded $\approx 0.145$ $\mu_B$. For continuity in the spin trajectories, continuous convergence was achieved with the preconditioned conjugate gradient algorithm (VASP ALGO=A). The first picosecond of every AIMD run was excluded from analyses for thermostat equilibration. The simulations at 100 K and 200 K, where sampling transitions requires long trajectories, were initialized by cooling from 300 K over 500 fs or longer. AIMD simulations with a Ni$_{Li}$ defect were initialized with the starting spin of the antisite Ni set to -2 $\mu_B$, and all others as default (1 $\mu_B$). The trajectories of the nickel spins were binned into $S = 0$, $S = 1/2$, and $S = 1$ states by milestoning [40] with cutoffs of 0.2 $\mu_B$, 0.7 $\mu_B$, 1.02 $\mu_B$, and 1.4 $\mu_B$.

A control simulation in the isobaric ensemble was carried out with the Langevin thermostat in VASP. The Ni-O vibrations at $\approx$15 THz were an effective degree of freedom to which to couple the random force of the thermostat, but such thermostatting strongly perturbed the dynamics of the Ni-O bonds. Instead, only the Li ions were coupled to the thermostat with a Langevin constant 12 ps$^{-1}$, and Ni and O were left as Newtonian.

The defect formation energies were calculated only for charge-neutral structures from relaxed defect-free and defect-incorporating cells [41–44]. The chemical potentials of the elements at synthesis conditions were calculated from the energies of the reference phases [44–46]. At the typical conditions of synthesis—1 atm O$_2$ pressure and 700 C—the chemical potential of oxygen is $\mu_{O} = -1.065$ eV, which determines $\mu_{Li} = -2.954$ eV and $\mu_{Ni} = -1.343$ eV (Figure 4(a)). We account for the antiferromagnetic–paramagnetic transition of NiO at its Néel temperature, taking the energy of paramagnetic NiO as the average of computed AFM and FM configurations. We have used the scientific Python computing stack [47–50] and pymatgen [51] in performing analyses.
Disproportionation

The relaxed energy of the commonly accepted zigzag P2_1/c phase is 83 meV/f.u. below the bulk-average R̅3m phase, consistent with previous studies [11]. However, for relaxations of ionic geometry starting with the R̅3m phase we find a partial disproportionation of pairs of Ni spins from $S = \frac{1}{2}$ to $S = 1$ and $S = 0$ for all meta-GGA functionals. If all $S = \frac{1}{2}$ nickels are consumed and the resulting ($S = 1$, $S = 0$) pairs ordered, such disproportionation yields the previously computationally predicted P2/c phase [11,12,52]. We note, however, the similarity between the three interpenetrating transition-metal sublattices in the ground state of Li(NiMnCo)O_2 [53], the ground state of the noncollinear spins model [3], and the disproportionated structure of AgNiO_2 [8,9], which each exhibit three interpenetrating sublattices. This suggests that the true endpoint for disproportionation is a phase where nickels with spins $S = 1$, $S = \frac{1}{2}$, and $S = 0$ similarly occupy three sublattices (Figure 1), as first proposed by Foyevtsova et al. [12].

When this trigonal three-spin structure is relaxed, the volumes of the NiO_6 octahedra correlate with the spin of the nickels: 10.8 Å³ for $S = 1$, 9.9 Å³ for $S = \frac{1}{2}$, and 9.0 Å³ for $S = 0$ (Figure 1), similar to AgNiO_2. All octahedra are somewhat distorted. The longest relaxed Ni–O bond is 2.06 Å, which is shorter than the Ni–O distance of 2.10 Å obtained in the P2_1/c structure. When starting from the R̅3m unit cell, a small (< 1 degree) distortion appears during relaxation. This relaxed disproportionated structure and the P2/c phase have energies 12 meV/f.u. and 14 meV/f.u. above the zigzag P2_1/c phase, respectively. However, configurational entropy is expected to favor this disproportionated structure and other intermediate compositions over the P2_1/c and P2/c endpoints. The energetic penalty for changing the ordering of the three sublattices of adjacent NiO_2 layers is 5 meV/f.u., and antiferromagnetic (AFM) or ferrimagnetic (FiM) orderings carry penalties of ≈1 meV/f.u.

Figure 1: Schematic of NiO_6 sublattices in LiNiO_2 with the $\sqrt{3} \times \sqrt{3}$ unit cell (yellow), and NiO_6 bond lengths.
We next investigate the spin and lattice dynamics of defect-free LiNiO$_2$ using AIMD simulations. An example trajectory of nine Ni magnetic moments within one NiO$_2$ layer at 300 K using the symmetric hexagonal cell (Figure 2(a)) shows the disproportionation of pairs of $S = \frac{1}{2} (\approx 0.86 \mu_B)$ nickels to $S = 1 (\approx 1.57 \mu_B)$ and $S = 0$ (near 0 $\mu_B$), e.g. at $\approx 420$ fs, and the reverse process of comproportionation, e.g., at $\approx 650$ fs. Additional coupled motions of spins, where the spin of one nickel decreases by $\frac{1}{2}$, and the spin of another Ni increases by $\frac{1}{2}$, such as at $\approx 50$ fs and $\approx 900$ fs, are reminiscent of small-polaron conduction. More complex motions of multiple spins are also seen, e.g., at 300 fs–400 fs. The longer trajectories of three nickel spins and their NiO$_6$ volumes in Figure 2(b) verify the coupling between the nickel spins and NiO$_6$ volumes. The volume coordinate is more noisy, with the major oscillatory components $\approx 15$ THz between the major Raman-active resonances of LiNiO$_2$ [23].

![Figure 2](image)

**Figure 2:** Trajectories of Ni spins and polyhedral volumes from ab initio molecular dynamics simulations. (a) all Ni spins in a nine-nickel layer at 300 K over 1 ps, (b) spins and NiO$_6$ volumes for three of the nine nickels in (a) over 10 ps.
We next examine the energetics of spin and lattice motions from the AIMD trajectories. We construct the free energy (F) surfaces from trajectories using \( F(q) = -k_B T \ln(p(q)) \), where \( p(q) \) is the probability distribution over a set of coordinates \( q \), and \( k_B \) and \( T \) are Boltzmann’s constant and temperature, respectively. Here we use the Ni magnetic moments and NiO\(_6\) volumes as two such coordinates, illustrating their coupling at 300 K (Figure 3(a)). These two simple coordinates do not account for the two-body nature of disproportionation; a coordinate accounting for the requisite pairings of neighboring nickels would do so more rigorously. We use single-Ni coordinates here for simplicity. The lowest-energy paths between the \( S = 1 \) and \( S = \frac{1}{2} \) states, and between the \( S = 0 \) and \( S = \frac{1}{2} \) states, take \( \approx 100 \) meV relative to the \( S = \frac{1}{2} \) minimum. The lowest-energy transition path between \( S = \frac{1}{2} \) and \( S = 0 \) is narrower than that between \( S = \frac{1}{2} \) and \( S = 1 \). Because of the flatness of the 2D surface near the saddle point between \( S = \frac{1}{2} \) and \( S = 1 \), projections onto the spin coordinate alone (Figure 3(b)) slightly underestimate the saddle point energies from the two-dimensional space. However, the 1D projections serve to illustrate temperature trends: in these simulations, disproportionation becomes less favorable with increasing temperature. Although the average concentrations of \( S = 1 \) and \( S = 0 \) nickels decrease

![Figure 3: Free energy surfaces for the Ni spin dynamics simulated with r\(^2\)SCAN+rVV10 and the R\(\overline{3}m\) cell: (a) At 300 K, versus Ni magnetic moments and NiO\(_6\) octahedral volume, (b) versus Ni magnetic moments alone. The arrows connecting panels (a) and (b) highlight saddle points.](image-url)
upon heating, the transitions between them become more frequent. The existence of saddle points, and the increase in their energies with heating (Figure 3(b)) are consistent with the thermal activation of electronic conductivity and an activation energy that rises upon heating.

**Polarons and Antisite Defects**

We next explore the possible influence of disproportionation on defect chemistry, starting with the localization of electronic charge carriers and the intrinsic antisite defect. We have relaxed hole and electron polarons in the disproportionated structure by distorting the octahedra of a $S = ½$ nickel to the sizes commensurate with $S = 0$ for the hole and $S = 1$ for the electron. While distortions of neighboring octahedra are minimal, some relaxations instead yield a reordering of the Ni spins and their respective octahedral volumes from the original three-sublattice ordered structure (Figure 1). These results are consistent between 108-atom and 144-atom supercells. The stabilization of polarons is consistent with a qualitative correspondence between the presence of extra charges and changes in the nickel spin-state; the precise extent of polaron localization and the participation of oxygen ligand states in charge dynamics are beyond the scope of this work. By contrast, we have not been able to stabilize a hole polaron or a nickel with spin near zero in the zigzag P2$_1$/c structure at the meta-GGA level of theory. The only condition with which we have been able to relax a hole polaron and $S \approx 0$ in the P2$_1$/c structure was with a 2×3×2 supercell (96 atoms) and surrounded by six opposite-sign $S = -½$ spins on adjacent nickels, which forms a superlattice like the disproportionated one discussed here. This arrangement is clearly artificial, is energetically unfavorable relative to a delocalized hole, and is not stabilized in other supercells. The electron polaron is stable on a $S = 1$ nickel in the P2$_1$/c structure, consistent with earlier work, which carried out the geometry relaxation at the hybrid level of theory [44].

We now examine the Ni$_{Li}$ antisite defect. Within spin-disproportionated structures, there are multiple possible configurations for the Ni$_{Li}$ antisite depending on the arrangements of the nickel spins adjacent to it within the NiO$_2$ layers. To calculate the absolute defect formation energies, we first determine the chemical potentials of the elements from reference phase energies [46] (Figure 4(a)). Accounting for the paramagnetic transition of NiO and representing the energetics of NiO accurately (Table 1) are key to the accuracy of estimating $\mu_{Li}$ and $\mu_{Ni}$. 

**Figure 4**: defect energetics in LiNiO$_2$. (a) Region of phase stability for LiNiO$_2$, with the synthetic conditions denoted with the yellow circle. (b) Energies of formation for the Ni$_{Li}$ antisite defect in the zigzag P2$_1$/c and disproportionated (‘disprop’) phases at synthesis conditions, and its antiferromagnetic stabilization by $S=1$ nickels.
which factor into the calculation of the absolute defect formation energy. The phase equilibrium at synthesis is between LiNiO₂ and the computationally predicted LiNi₂O₃ [54]. This is consistent with the experimental synthesis pathway from NiO via lithium insertion through a sequence of rock salt phases with intermediate Li concentrations followed by layer formation [55]. Finally, as Li₂NiO₃ is not easily synthesized [56], and not observed as a decomposition product, we ignore Li₂NiO₃ when bounding the stability region of LiNiO₂ (grey in Figure 4(a)).

At synthesis conditions, the lowest-energy configuration for the Ni₁₁̅ defect is one where a S = -1 Ni₁₁̅ sits on a straight line connecting two S = 1 nickels via 180° Ni–O–Ni motifs (Figure 4(b)), reminiscent of antiferromagnetic NiO. This configuration, as well as several others, has a lower energy than the Ni₁₁̅ defect in the P2₁/c structure, where only one NiNi carries S = 1 to compensate the Ni₁₁̅. At synthesis conditions, the absolute formation energies for these configurations are under 100 meV (Figure 4(b)) due to stabilization by antiferromagnetic Ni–O–Ni interactions. Our estimate of the formation energies for the most stable local configurations of Ni₁₁̅ is lower than reported earlier [44] due to three factors: accounting for the paramagnetism of NiO, using a different DFT functional to account for the formation energy of NiO, and accounting for the possibility of disproportionation in LiNiO₂. While the local atomic and spin arrangements are expected to fluctuate rapidly at synthesis, the results remain relevant for lower-temperature degradation pathways during battery operation.

From AIMD trajectories at 300 K and 500 K incorporating a Ni₁₁̅ antisite, the nickels sharing octahedral corners with the defect as in Figure 4(b) carry S = 1 on average 50% more time than nickels away from the defect: the S = 1 that compensate the antisite are not free even at elevated temperatures. Here we show that magnetic stabilization contributes to the ubiquity of this pervasive defect. Ni₁₁̅ is stable not only because of the size match between Ni and Li, but also because of the ability of the Ni to disproportionate in the layered structure, which distinguishes it from Co and Mn. This effect may also contribute to the driving forces for surface reconstructions and nickel migration into the lithium layer during charging.

Sensitivity Analysis

The dynamics of disproportionation are sensitive to the simulation setup. First, we compare the free-energy surfaces from the reference simulation performed with a 2×2×2 k-point mesh (Figure 5(a), blue) versus a simulation performed at the Γ point exclusively (Figure 5(a), pink). The two surfaces are drastically different: the Γ-point simulation does not predict stable disproportionation or any activated dynamics. In the Γ-point simulation, magnetic moments below 0.2 μB or above 1.5 μB are not realized. Figure 5(a) also shows that a small distortion of the cell angles acquired during the relaxation of the three-spin disproportionated structure (Figure 1) perturbs the energy surface (Figure 5(a), purple), making transitions slightly rarer relative to the symmetric hexagonal high-temperature cell (Figure 5(a), blue). Performing the simulation in the isobaric ensemble has a similar effect (Figure 5(a), green), and using a larger cell with 144 atoms instead of 108 as in all the other runs (Figure 5(a), orange) predicts smaller saddle-point energies.

However, the simulation results are most sensitive to the choice of functional. Using the SCAN functional (Figure 5(b)) yields a temperature-independent set of free-energy surfaces. Using SCAN favors all-spin-half arrangements upon cooling, as predicted earlier [11], while r²SCAN
favors disproportionation at cryogenic temperatures. The results from all functionals ($r^2$SCAN and SCAN+rVV10 not shown) agree best at high temperatures and disagree most towards cryogenic temperatures. This can be seen in the projections onto the NiO$_6$ octahedral volumes in Figure 5(c) for $r^2$SCAN+rVV10 and Figure 5(d) for SCAN. This behavior of the simulated dynamics follows the trends in matching the thermodynamics of NiO and LiNiO$_2$ (Table 1); the choice of functional dominates the non-local corrections. We hypothesize that the high sensitivity to the choice of functional is due to the relative energy differences under investigation (<20 meV/f.u. between disproportionated and P2$_1$/c structures) being smaller than the energies of relevant phonons (>60 meV) and the differences in predicted formation energies between functionals (e.g., 0.3–0.4 eV/f.u. for NiO, Table 1). This may represent a limit of precision for computational studies of LiNiO$_2$ structure and dynamics.

![Figure 5: Sensitivity of simulated free energy surfaces to simulation parameters.](image)

Figure 5: Sensitivity of simulated free energy surfaces to simulation parameters. (a) free energy surfaces versus the Ni magnetic moment with $r^2$SCAN+rVV10 at 300 K: reference as in Figure 3 (blue), relaxed cell with a small distortion (purple), hexagonal cell at the $\Gamma$ point only (pink), hexagonal cell with 144 atoms (green), and simulation in the isobaric ensemble (orange). (b) free energy surfaces versus the Ni magnetic moment with SCAN and the hexagonal cell. (c-d) free energy surfaces versus the NiO$_6$ volume with $r^2$SCAN+rVV10 (c) or SCAN (d) and the hexagonal cell.

Ultimately, computational predictions such as ones put forward here require additional experimental verification. Both the experimental studies highlighted above, and our computational predictions suggest that the material itself changes substantially and gradually between cryogenic, ambient, and synthesis temperatures. The sensitivity analysis above assists in finding probative experiments to verify the computational predictions. We expect structural probes (diffraction, PDF) to be most probative towards cryogenic temperatures, as exploited by Foyevtsova et al. [12]. We expect data from structural probes to become harder to interpret for
distinguishing local chemistry at room and elevated temperatures because of the dynamical broadening of bond distances, the multitude of possible bond distances, and the poor separation of the various states along the structural coordinate (Figure 5(c)–(d)). Bulk-sensitive core-level spectroscopic probes should retain sensitivity, however, due to the more effective separation of nickel states along the magnetic coordinate (Figure 3) and the possibility for distinguishing states along additional coordinates such as energy loss in inelastic X-ray scattering [57]. Therefore, we expect self-consistent spectroscopic data sets spanning cryogenic to ambient temperatures to potentially offer a more complete picture of LiNiO₂. Finally, given the other experimental trends reviewed above, and the computational evidence presented here, we expect the optical band gap to also have a strong temperature dependence.

Conclusions and Outlook

Here we have investigated the possibility of temperature-dependent dynamic disproportionation in the model layered cathode LiNiO₂. Simulations predict that at low temperatures the formally 3d⁷ spin-half nickels in LiNiO₂ exhibit three stable states with spins \( S = 0, S = \frac{1}{2}, \) and \( S = 1 \), and interconvert between them on a picosecond timescale. This computational prediction is consistent with measured heat-activated electronic conductivity, cryogenic neutron diffraction data, magnetometry, and other data demonstrating gradual changes in the properties of LiNiO₂ between cryogenic and ambient temperatures. The ability of Ni to disproportionate in the layered structure provides additional AFM stabilization for the Ni\(_{\text{Li}}\) antisite defect by \( S = 1 \) nickels and contributes to degradation via nickel migration and surface reconstruction during battery cycling. The main driving forces behind the peculiar defect chemistry are covalency, which allows disproportionation, and strong NiO-like AFM coupling, also enabled by covalency. Disproportionation may further explain the stoichiometric ranges for single-phase and two-phase regimes upon delithiation: e.g., 22% removal of Li where the M-H1 two-phase region starts [27] corresponds to 2/9 Li being removed from a unit cell with 3×3 Ni in each layer.

However, our computational predictions are sensitive to the choice of DFT functionals despite the relatively small differences between the functionals used. We propose that temperature-resolved bulk-sensitive spectroscopies are best positioned to provide probative experimental data to verify our computational predictions. Structural probes are likely to yield unambiguously interpretable data only at cryogenic temperatures. Additional questions remain regarding the precise electronic structure of valence-band holes among Ni and O orbitals and the nature of the optical band gap.

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