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Electronic structure and vacancy formation of Li$_3$N

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The electronic structure and vacancy formation of Li$_3$N were studied using first principles methods. We found Li$_3$N exhibits strong ionic character with slight covalent bonding between N and Li. The Li vacancy formation energy decreases with an increase in nitrogen partial pressure, while the N vacancy formation energy increases with increasing nitrogen partial pressure. The Li(2) site vacancy is found to have the lowest formation energy under nitrogen-rich conditions. Formation of V$_{Li(2)}^-$ brings about delocalization of valence electrons, and reduces the band gap by 0.2 eV. These results suggest potential ways to enhance vacancy concentration in Li$_3$N for higher ionic conductivity.

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Li$_3$N has an exceptionally large Li ionic conductivity due to intrinsic defects and the resulting hopping of Li ions from occupied Li sites into unoccupied ones. The nature of the defect plays a critical role in the understanding and application of the material for hydrogen storage and lithium batteries. Li$_3$N can be described as a sequence of Li atoms, and result in an energetically very unfavorable N$_2^-$ ion. The nature of the vacancy formation energy increases with increasing nitrogen partial pressure. The Li(2) site vacancy is found to have the lowest formation energy under nitrogen-rich conditions. Formation of V$_{Li(2)}^-$ brings about delocalization of valence electrons, and reduces the band gap by 0.2 eV. These results suggest potential ways to enhance vacancy concentration in Li$_3$N for higher ionic conductivity.

\[ E_F(V^0) = E_F(V^0) - E_F(V_{Li(2)}^+) + \mu_i + q(VBM + \Delta V + e_F), \tag{1} \]

where $E_F(bulk)$ and $E_F(V^0)$ are the total energy of the defect-free supercell and the supercell with vacancy at charge state $q$, respectively; $\mu_i$ is the chemical potential of the atom removed from the supercell to form the vacancy; $e_F$ is the Fermi energy measured with reference to the valence band maximum (VBM). The correction term $\Delta V$ aligns the reference (GGA) parameterized by Perdew et al.\textsuperscript{13,14} In our pseudopotential, $2s$ and $2p$ for Li and $2s$ and $2p$ for N were treated as valence. All atoms in the supercells were free to move in the geometry optimization. The electronic structure of the perfect Li$_3$N crystal was investigated with primitive cell and $11 \times 11 \times 11$ $k$-point mesh according to the Monkhorst-Pack scheme.\textsuperscript{15} The optimized lattice constants $a = 3.65$ Å and $c = 3.88$ Å are consistent with the experimental values, 3.64 and 3.87 Å.\textsuperscript{2,3} Li$_3$N supercells of 108 atoms were constructed for vacancy calculations by $3 \times 3 \times 3$ expansion of the unit cell. $4 \times 4 \times 4$ $k$-points (the Monkhorst-Pack method) were selected in supercell calculations. Convergence with respect to $k$-points and energy cutoff was checked during all calculations.

The formation energy of a charged vacancy $E_F(V^0)$ is defined as

\[ E_F(V^0) = E_F(V^0) - E_F(V_{Li(2)}^+) + \mu_i + q(VBM + \Delta V + e_F), \tag{1} \]

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The formation energy of a charged vacancy $E_F(V^0)$ is defined as

\[ E_F(V^0) = E_F(V^0) - E_F(V_{Li(2)}^+) + \mu_i + q(VBM + \Delta V + e_F), \tag{1} \]
The chemical potential \( \mu_i \) depends on crystal growth conditions such as the nitrogen partial pressure. The valid range of \( N_2 \) partial pressure \( P_{N_2} \) is determined by Li3N formation enthalpy \( \Delta H_f^{\text{Li3N}} \):

\[
\frac{\Delta H_f^{\text{Li3N}}}{RT} \leq \ln P_{N_2} \leq 0 \quad \text{with} \quad \Delta H_f^{\text{Li3N}} = 3(\mu_{\text{Li}} - \mu_{N}) + (\mu_{N} - \mu_{N}^0),
\]

where \( \mu_{\text{Li}} \) and \( \mu_{N} \) are the chemical potential of Li and N in Li3N, respectively; \( \mu_{\text{Li}}^0 \) and \( \mu_{N}^0 \) are the energy of metallic Li and gaseous \( N_2 \) (per nitrogen atom) in the standard state; \( k \) is the Boltzmann constant; and \( T \) is the temperature. The Li3N formation enthalpy is calculated to be \(-1.59 \text{ eV per Li3N}\), which is within the typical GGA errors from experimental value of \(-1.73 \text{ eV per Li3N}\).

The calculated electronic band structure and density of states (DOS) of the defect-free Li3N are shown in Fig. 2. The VBM and conduction band minimum (CBM) are located at A and \( \Gamma \), separately, giving an indirect gap consistent with previous experimental and theoretical reports. The calculated band gap is 1.1 eV, which is underestimate by 1.1 eV as compared with the measured value.\(^{19}\) The band around \(-11.5 \text{ eV}\) is dominated by N 2s state with a Li 2s and 2p admixture. The conduction bands are mainly composed of Li 2s and 2p states and the occupied valence bands originate from N 2s and 2p states. The partial overlapping of Li 2s state with N 2p state in the valence band region suggests possible Li(1)–N and Li(2)–N s-p covalent bonds. The different characteristics of \( p_x, p_y, \) and \( p_z \) states of N atom indicate the anisotropy of the structure. Employing Bader’s “atoms in molecules” scheme,\(^{20}\) we obtained nominal valences of N\(^{2+}\), Li(1)\(^{3+}\), and Li(2)\(^{3+}\). This further suggests covalent bonding between Li and N. This is consistent with the real-space multi-scattering (RSFMS) calculations by Fister et al.\(^{7}\)

The formation energies of all major intrinsic vacancies in Li(1), Li(2), and N sites calculated with Eq. (1) are shown in Fig. 3 as a function of Fermi level at N-rich condition (i.e., \( \mu_N = \mu_{N}^0 \)). The Li(2) site vacancies are located in N-containing layers, while the Li(1) site vacancies lie in the layers between these N-containing layers (Fig. 1). Li(2) site vacancy shows the lowest formation energy, which is consistent with experimental observations.\(^{5,6}\) The negative \( V_{\text{Li}(2)} \) vacancy is the most abundant vacancy with the formation energy as low as \(-1.5 \text{ eV}\), indicating that thermal generation of vacancies is important even at low temperature in agreement with experimental report.\(^{1}\) The high concentration of Li(2) site vacancy is believed to contribute significantly to the unusually large ionic conductivity of Li3N since it provides pathways for Li ion hopping. An increase in Li vacancy concentration corresponds to high Li ion mobility and thus high ionic conductivity.\(^{21}\) The vacancy formation energy in the Li(1) site is about 1.7 eV higher than that in the Li(2) site. Therefore, removal of the lithium between the Li3N layers is a very energetically unfavorable process since the two nearly triply negative nitrogen ions would now be repelled by their own ionic charges and by the effective negative charge of \( V_{\text{Li}(1)} \) vacancy. The formation energy of neutral nitrogen vacancies is the highest. Even the most stable \( V_{\text{N}}^3 \) vacancy among possible N vacancies has a formation energy that is about 1.0 eV higher than that of \( V_{\text{Li}(2)} \). This indicates that the nitrogen vacancies rarely exist under N-rich conditions.

The vacancy formation energy as a function of nitrogen partial pressure is shown in Fig. 4 for two characteristic Fermi levels, VBM and CBM. Atmospheric nitrogen conditions determine the type and concentration of vacancies in Li3N. When the Fermi energy is set at the VBM, \( V_{\text{N}}^2 \) and \( V_{\text{Li}(2)} \) may form. The difference in formation energy of \( V_{\text{N}}^2 \) and \( V_{\text{N}}^3 \) is only 0.01 eV, and consequently they have similar concentrations. The formation energy of N vacancies increases with an increase in nitrogen partial pressure, while the formation energy of Li vacancies decreases with an increase.
Formation of charged vacancies in Li$_3$N brings about a significant change in band structure. $V_{\text{Li}(2)}$ vacancy splits the peak at about $-11$ eV into two peaks with separation of 0.3 eV. The accompanying highly splitted $p_x$, $p_y$, and $p_z$ states indicate valence electron delocalization, and thus enhance conductivity. The vacancy charge is unevenly distributed among all atoms with the neighboring N atoms allocated the largest portion. This brings about a decrease in the gap between VBM and CBM by $-0.2$ eV. Conversely, the formation of $V_{\text{N}}^{3+}$ in the structure expands the gap by 0.2 eV. The $p_z$ state exhibits moderate splitting, indicating valence electron delocalization in Li$_2$N layers. This increases the anisotropy of conductivity. The alternation of band structure with vacancy implicates additional controlling of Li$_3$N conductivity via vacancy selection.

In conclusion, first-principles calculations suggest that vacancies in Li$_2$(2) sites are responsible for the experimentally observed apparent nonstoichiometry of Li$_3$N. The vacancy formation energy at Li$_2$(2) sites decreases with an increase in nitrogen partial pressure. Since the vacancies in the Li$_2$(2) sites are responsible for the conductivity of Li$_3$N, nitrogen-rich condition is preferred for Li$_3$N fabrication process to attain high vacancy concentration and thus conductivity. Under extreme conditions, the dominant $V_{\text{Li}(2)}$ vacancy reaches formation energy as low as $-1.50$ eV. Such low formation energy suggests that thermal generation of vacancies plays an important role in controlling vacancy level and therefore conductive mechanism. Formation of $V_{\text{Li}(2)}$ brings about valence electron delocalization and thus enhances the ionic conductivity. These results enhance our understanding of the physics of intrinsic defects and potential measure to control the vacancy in Li$_3$N and its derivatives.

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