Nanointerface-Driven Reversible Hydrogen Storage in the Nanoconfined Li–N–H System


Dedicated to Natchapol “Golf” Poonyayant, who died tragically at the age of 25 during the writing of this paper. Golf’s interest in nanoconfined materials inspired this work, and he performed the experimental synthesis and much of the analysis. The world has lost a talented young man, and we have lost a dear friend.

Hydrogen is an excellent energy carrier, yet the development of lightweight solid-state materials for compact, low-pressure storage remains challenging.[1] Nanoconfinement can improve the hydrogen-storage viability of complex metal hydrides, with enhancements typically attributed to shortened diffusion pathways or surface-driven stability changes.[2,3] However, the equally important role of internal interfaces in these storage remains challenging.

For more than a decade, LiNH$_2$ has been investigated as a potential material for lightweight and compact solid-state hydrogen storage, as it can participate in high-capacity reactions when combined with binary metal hydrides such as LiH[4–7] or MgH$_2$.[8] Chen et al.[8] first reported the hydrogen-storage performance of bulk α-Li$_2$N, which hydrogenates to [LiNH$_2$ + 2LiH] via a two-step reaction pathway

$$\alpha$$-Li$_2$N + H$_2$ ⇔ Li$_2$NH + LiH

(1)

Li$_2$NH + LiH + H$_2$ ⇔ LiNH$_2$ + 2LiH

(2)

The combined sequence possesses a theoretical gravimetric density of 10.4 wt% H, and as written avoids the ammonia release associated with dehydrogenation of bulk LiNH$_2$.[5,6] It is well documented that the bulk material suffers from poor reaction kinetics.[9] Initial hydrogen release from the bulk [LiNH$_2$ + 2LiH] mixture commences at ≈150 °C and reaches a maximum at ≈245 °C; however, the stability of the bulk intermediate [Li$_2$NH + LiH] prevents further dehydrogenation until the temperature is raised to ≈430 °C.[6]

The precise microstructure during hydrogenation/dehydrogenation is difficult to determine since it depends on the conditions and progress of the reaction, and the constituent light elements are easily damaged by electron beam probes (Supporting Information). Nevertheless, a sensible rendering of the microstructure evolution can be generated based on prior studies.[4,6,10–18] As shown in Figure 1, the nitrogen-containing phases likely form a core–shell structure with contiguous, mobile LiNH$_2$/Li$_2$NH and Li$_2$NH/Li$_2$N interfaces. The lattice contiguity of these N-containing phases is suggested by crystallographic similarities between LiNH$_2$ and Li$_2$NH pointed out by David et al.[15] and by the high formation energies and diffusion barriers for NH$_4$ defects in LiNH$_2$ and Li$_2$NH that inhibit the possibility of N interdiffusion.[11] In addition, the inference of nonstoichiometric Li/H compositions (i.e., Li$_{1+x}$NH$_{2-x}$) within the LiNH$_2$ and Li$_2$NH parent phases,[10,12,13] combined
with the predicted facile interdiffusion of Li and H\(^{[10,14]}\) suggest that Li and H compositions within the N-containing phases vary continuously along oppositely oriented chemical potential gradients. During hydrogenation, outer regions of the particle that are exposed to H\(_2\) gas will therefore tend to be H-rich and Li-lean, and vice versa during dehydrogenation. The core–shell model microstructure in Figure 1 is generally consistent with previously proposed models.\(^{[17]}\)

One can further assume that LiH appears throughout the Li\(_2\)NH and LiNH\(_2\) phases. During initial hydrogenation (Figure 1a), LiH should begin in an embryonic state with dimers or clusters in a solid solution or nonstoichiometric mixture\(^{[13]}\) (panel (i)). Multiple crystallites will then nucleate and grow along the reaction front (panel (ii)) before finally coarsening (panel (iii)). Dehydrogenation follows the reverse pathway. Smaller particles favor the dispersed LiH state (i) due to interfacial penalties associated with nucleation.

Changes in hydrogenation kinetics of Li\(_3\)N upon confinement were first reported by Demir-Cakan et al.\(^{[20]}\) who showed that enhancements could be achieved with Li\(_3\)N derived from decomposition of lithium azide in mesoporous carbon. However, the explosive nature of the decomposition introduces synthetic safety risks upon scale-up and could potentially damage the structural integrity of the nanoscaffold. Instead, we base our investigation on a new and improved synthetic route that involves dissolution of metallic lithium in liquid ammonia\(^{[21]}\) followed by the infiltration of the Li(NH\(_3\))\(_2\) solution into a nanoporous carbon (npC) host. Subsequent evaporation of ammonia from the solvated complexes results in formation of nanoconfined LiNH\(_2@\)npC, which forms Li\(_3\)N@npC when heated in vacuum at 340 °C. The overall sequence can be written:

![Figure 1. Schematic microstructure of the [LiNH\(_2\)+2LiH]/[Li\(_2\)NH+LiH]/Li\(_3\)N system. Panels (a) and (b) indicate Hydrogenation and dehydrogenation, respectively. The nitrogen-containing phases (blue = LiNH\(_2\), pink = Li\(_2\)NH, gray = Li\(_3\)N) form a contiguous core–shell structure with phase boundaries propagating along the directions indicated by small arrows. a) During hydrogenation, LiH (green) is assumed to evolve from (i) a dispersed molecular, cluster, or solid-solution state to (ii) nucleated crystallites that eventually (iii) coarsen. b) Dehydrogenation follows the reverse pathway. Smaller particles favor the dispersed LiH state (i) due to interfacial penalties associated with nucleation.](image-url)
[Li (s) + NH_3 (l)]@npC → Li(NH_3)_x@npC → LiNH_2@npC → Li_3N@npC (see the Experimental Section). We used a npC host with an average pore size of 3.2 nm from porosimetry analysis (Figure S1, Supporting Information) and a Li_3N loading of 39.2 wt% from elemental analysis (Table S1, Supporting Information).

**Figure 2.** Characterization of reaction products. a) PXRD patterns of (i) bulk LiNH_2; (ii) as-synthesized nanoconfined LiNH_2@npC; and the synthesized material cycled at 250 °C ending in (iii) hydrogenated, (iv) dehydrogenated, and (v) half-dehydrogenated states. Crystalline phases are indicated by symbols: (*) for LiNH_2, (A) for LiH, and (o) for β-Li_3N. b) NVS at −269 °C for reference samples of (i) Li_2NH, (ii) LiNH_2, (iii) LiH, and the synthesized cycled material ending in (iv) hydrogenated and (v) dehydrogenated states. c) Sieverts and d) FTIR data for half-dehydrogenated LiNH_2@npC. In (d), FTIR data for empty npC and a bulk reference sample of authentic LiNH_2 are shown for comparison; these are shifted vertically for clarity of presentation but have not been scaled.

[Li (s) + NH_3 (l)]@npC → Li(NH_3)_x@npC → LiNH_2@npC → Li_3N@npC (see the Experimental Section). We used a npC host with an average pore size of 3.2 nm from porosimetry analysis (Figure S1, Supporting Information) and a Li_3N loading of 39.2 wt% from elemental analysis (Table S1, Supporting Information).

**Figure 2a** shows powder X-ray diffraction (PXRD) for the as-synthesized LiNH_2@npC (Figure 2a(ii)) before conversion to Li_3N@npC. Comparison with the reference pattern for bulk LiNH_2 (Figure 2a(i)) confirms that LiNH_2 is the only crystalline phase present. Porosimetry measurements indicate a large decrease in the surface area and pore volume of npC upon infiltration, confirming that the active material is indeed inserted inside the nanopores (see the Supporting Information and Figures S2 and S3, Supporting Information).

The as-synthesized LiNH_2@npC material was heated to 340 °C in a Sieverts apparatus and then subjected to hydrogen cycling at temperatures up to 250 °C. Fully reversible hydrogenation/dehydrogenation was observed (Figure 3) with uptake of ≈4 wt% H relative to the mass of the sample, that is, including the mass of the inert npC scaffold. This translates to the active material cycling reversibly at ≈10.3 wt% H, consistent with the theoretical capacity of complete interconversion between [LiNH_2 + 2LiH] and Li_3N. Moreover, the nanoconfined [LiNH_2 + 2LiH]@npC material exhibited almost no capacity loss after five reversible cycles, indicating irreversible ammonia release associated with bulk LiNH_2 decomposition was suppressed (further confirmed by mass spectrometry; see Figure S4, Supporting Information). Elemental analysis of the hydrogenated and dehydrogenated materials indicated compositions of Li_3N_0.85N_1.15 and Li_3N_0.85N_1.15, respectively, very close to expected ratios for [LiNH_2 + 2LiH] and Li_3N (Table S1, Supporting Information). The PXRD patterns (Figure 2a) and neutron vibrational spectra (NVS; Figure 2b) of the material following hydrogenation (Figure 2a(iii),(iv)) and dehydrogenation (Figure 2a(iv)–(v)) further confirm that cycling between crystalline [LiNH_2 + 2LiH] and Li_3N is complete (note that NVS is dominated by H-derived vibrational modes and is sensitive to noncrystalline phases). Interestingly, the exclusive presence of LiNH_2 and LiH following hydrogenation means that the material has self-optimized upon thermal cycling, converting the as-synthesized LiNH_2@npC to the high-capacity [LiNH_2 + 2LiH]/Li_3N@npC system. Hydrogen cycling of [LiNH_2 + 2LiH]/Li_3N@npC (Figure 3a) shows smooth absorption/desorption curves without...
in the PXRD patterns at the hydrogenated (Figure 2a(iii)) or dehydrogenated (Figure 2a(iv)) ends after cycling at 250 °C, despite the fact that this temperature is well within the stability range of bulk [Li₂NH + LiH]. Similarly, NMR measurements confirm that the hydrogenated system can be expressed as a graphical convolution of only the reference LiNH₂ and LiH spectra, and that no trace of Li₂NH is seen upon subsequent dehydrogenation to Li₁N@npC (Figure 2b(v)). Fourier transform infrared spectroscopy (FTIR) was used to investigate intermediate stages of dehydrogenation. Figure 2c shows a Siervets desorption and corresponding FTIR data for [LiNH₂ + LiH]@npC interrupted at ~2 wt% hydrogen (i.e., half dehydrogenation). Only LiNH₂ is present, with no evidence for Li₂HNH (strong absorption at 3100–3200 cm⁻¹). The PXRD pattern of the half-dehydrogenated sample (Figure 2a(v)) likewise indicates that LiNH₂ and β-Li₁N are the major species (along with a trace amount of LiH). These data conclusively demonstrate direct dehydrogenation of [LiNH₂ + 2LiH]@npC to Li₁N@npC, in agreement with Figure 2. As additional evidence that nanoco

Figure 3. Reversible hydrogen capacity and single-step reaction pathway of nanocoñfined [LiNH₂+2LiH]/Li₁N. a) Five consecutive absorption/desorption cycles of [LiNH₂+2LiH]@npC at 250 °C with the temperature profiles shown by black dashed lines. Absorption was performed at 100 bar H₂ pressure. The sample was cooled to room temperature before subsequent desorption (this process is omitted for clarity). The reported material wt% H is relative to the sample mass, including the inert npC. b) DSC of [LiNH₂+2LiH]@npC (blue), showing a single-step pathway compared with the two-step pathway of ball-milled [LiNH₂+2LiH] (black). DSC for a ball-milled mixture [LiNH₂+2LiH+C] with graphite at an equivalent mass ratio to that of [LiNH₂+2LiH]@npC is shown in red. For clarity, curves for [LiNH₂+2LiH+C] and [LiNH₂+2LiH] are shifted by −0.5 and −1.0 mW, respectively.

intermediate plateaus, pointing to a single rate-limiting step in lieu of the two-step sequence observed for the bulk system.

The elimination of the second rate-limiting step is also seen in differential scanning calorimetry (DSC; Figure 3b), where the results indicate that kinetic limitations ordinarily associated with Li₁NH decomposition are no longer relevant after nanoconfinement. This strongly suggests that Li₁NH never appears as an isolable intermediate phase and that the reaction proceeds rapidly to Li₁N within a single rate-limiting step. The temperature for the initial onset of hydrogen release is also significantly lowered (~150 °C) for the nanocoñfined sample even without catalyst addition. To exclude effects of any secondary chemical interaction with the confinement medium, DSC data were also obtained for bulk [LiNH₂+2LiH] ball-milled in the presence of graphite with a mass ratio equivalent to the nanocoñfined sample. Results reproduced the two-step mechanism of the bulk system, confirming that the influence of the nanoconfining medium is physical rather than chemical in origin.

Furthermore, there is no evidence of any residual Li₁NH intermediate (peaks at 30.45°, 51.14°, and 60.92°) in the limit of full dehydrogenation. In this case, no internal
interfaces are present, and nanoparticle stability is determined exclusively by single-phase bulk and surface energetics. As shown in Figure 4a, β-Li3N is indeed thermodynamically preferred over α-Li3N for particle diameters < 4.7 nm, a direct consequence of the lower effective surface energy of β-Li3N (0.66 J m⁻²) versus α-Li3N (0.73 J m⁻²).

On the other hand, surface energies of individual phases are unable to account for the elimination of the Li2NH phase that leads to a direct decomposition pathway; in fact, Li2NH has one of the lowest surface energies among the various phases (Table S3, Supporting Information). Instead, it is necessary to consider the implications of the relevant solid–solid interfaces between other coexisting phases (Figure 1), whose interface areas and energies depend on microstructure and reaction progress.

For small nanoparticles, we can make simplifying assumptions concerning the evolution of the microstructure during (de)hydrogenation. In particular, dispersed embryonic LiH (Figure 1, panel (i)) will manifest during much of the reaction, since the critical nucleus diameter for LiH (computed to be ≥2.4 nm; see Figure S11 and the accompanying discussion, Supporting Information) represents a large volume fraction of smaller nanoparticles. LiH crystallites will therefore manifest only at near-complete hydrogenation conditions. Accordingly, we focus our discussion on the microstructures in panel (i) of Figure 1, although the other two reaction stages (LiH nucleation and coarsening) are considered in Figure S8 (Supporting Information) and lead to similar conclusions.

Figure 4b,c shows the equilibrium phase fraction behavior predicted by our models for different H2 pressures mimicking (de)hydrogenation. These data are computed at 727 °C, which allows use of an ideal mixing model for phase coexistence (see the Experimental Section; analogous results at 250 °C require implementation of a nonideal mixing model, which is explored in Figure S12, Supporting Information, and shows the same qualitative behavior). Figure 4b confirms that suppression of the Li2NH intermediate phase becomes favorable at pressures relevant to hydrogenation (100 bar) and dehydrogenation (1 bar) for particles < 20 nm diameter. Moreover, the similarity in the hydrogenation and dehydrogenation pathways accounts for the reversibility of the LiNH2 + 2LiH ⇌ β-Li3N + 2H2 single-step reaction evidenced in Figure 3. Figure 4c shows the equilibrium phase fractions of Li3N, Li2NH, LiNH2, and LiH predicted for hydrogenation as a function of pressure for three different particle sizes (bulk, d = 10 nm, and d = 3.2 nm). The pressure range for Li2NH stability narrows as the particle size decreases, with the smallest particles (d = 3.2 nm) exhibiting an exceedingly thin stability range that disappears at H2 pressures > 10 bar. Under nonequilibrium conditions, this regime will be quickly bypassed and the likelihood of nucleating Li2NH will be negligible (Table S5, Supporting Information). This behavior explains the direct interconversion of Li3N and [LiNH2 + 2LiH] phases upon nanoconfinement. Larger particles, on the other hand, clearly express Li2NH at intermediate stages in the reaction cycle. Parallel results for dehydrogenation showing the same Li2NH phase suppression are provided in Figure S7 (Supporting Information).

Figure 4c also predicts higher phase purity after full cycling, in agreement with Figure 2: hydrogenation of the 3.2 nm diameter particle always gives an exact 2:1 LiH-to-LiNH2 ratio, whereas conversion remains incomplete for the bulk material even at higher pressures. This tendency may explain why the...
material self-optimizes to form [LiNH$_2$ + 2LiH]@npC upon initial cycling. Certain implications for improved kinetics can also be discerned. The phase fractions in Figure 4b transition much more abruptly at the nanoscale than in the bulk, suggesting a stronger driving force (and hence faster kinetics) for phase growth or depletion. Moreover, the elimination of Li$_3$NH as a solid phase necessarily increases the nonstoichiometric nature of LiH$_2$ during intermediate reaction stages, which has been shown to enhance mass transport kinetics in the latter material (LiH suppression should also have a similar effect). The effect of interfaces and surfaces is irrelevant in the bulk material from the interface free energies. As expected, the penalizing face effects are amplified by the coexistence of multiple phases.

To further establish that nanointerfaces drive the suppression of the Li$_3$NH intermediate phase, we computationally explored the sensitivity of the predicted phase fractions to contributions from the interface free energies. As expected, the penalizing effect of interfaces and surfaces is irrelevant in the bulk material but becomes increasingly severe as the particle size decreases (Figure S10, Supporting Information). Eventually, the Li$_3$NH phase is suppressed altogether in order to reduce the total number of interfaces within the nanoparticle, leading to direct hydrogenation and dehydrogenation. Moreover, nanoparticle simulations run without any interface contribution confirm that the presence of outer surfaces alone cannot account for the observed direct phase transformation pathway (Figure 4b).

In addition to the spherical particle geometry in Figure 1, calculations were also performed on a rod-shaped geometry nanoconfined material; see Figure S4, Supporting Information. The effective surface energies to induce Li$_3$NH suppression and reaction reversibility, carrying practical consequences for particle morphology engineering.

Beyond demonstrating [LiNH$_2$ + 2LiH]/Li$_3$NH@npC as a reversible, high-performing hydrogen-storage material, our work establishes that proper consideration of solid–solid nanointerfaces and particle microstructure is necessary for understanding hydrogen-induced phase transitions in complex metal hydrides. This highlights the analogy between hydrogen storage reactions and solid-state reactions in battery electrode materials, where internal interfaces have similarly been identified as important factors for altering phase transformation pathways. Significantly, this introduces the possibility of tuning solid-state hydrogen-storage materials by tailoring morphology and internal microstructure, representing a new paradigm for engineering materials that could meet established performance targets. Further gravimetric capacity improvements may also be achieved using emerging encapsulants with higher theoretical surface areas and loading ratios. Because nanointerface effects are amplified by the coexistence of multiple phases upon cycling, particularly prominent changes may be expected for nanoparticles with multicomponent mixtures.

### Experimental Section

**Synthesis of Li$_3$N@npC**: Synthesis and handling of air-sensitive materials were carried out under an Ar atmosphere using standard Schlenk line and glove box techniques. For npC synthesis procedure and porosimetry measurements, see the Supporting Information. Synthesis of Li$_3$N@npC began with the synthesis of LiH$_2$@npC. In a typical synthesis, 0.860 g of Li metal (99% pure from Aldrich) was placed in a Schlenk tube containing 3.109 g of activated npC. The tube was then suspended in a dry ice/acetonitrile bath at −78 °C. Under continuous flow of Ar, anhydrous ammonia gas (ultrahigh purity, Matheson) was fed into the tube and condensed to form ~20 mL liquid ammonia that completely covered the Li metal and npC. The mixture was stirred at −78 °C for 60 min to allow Li metal dissolution and infiltration, and the flask was left under a constant Ar flow so that liquid ammonia could slowly evaporate while the temperature gradually increased to room temperature for 16 h to yield LiNH@npC. This material was heated in vacuum at 340 °C to yield Li$_3$N@npC (through removal of NH$_3$ and H$_2$). Characterization details are given in Table S1 and Figures S1–S3 (Supporting Information).

**DFT Calculations**: DFT simulations were performed using Quantum Espresso with ultrasoft pseudopotentials based on the Perdew–Burke–Ernzenhof exchange-correlation functional. The plane-wave cutoff was 70 Ry and interatomic forces were converged to $<10^{-4}$ Ry Å$^{-1}$. Periodic bulk unit cells and internal coordinates for α-Li$_3$N (P6/mmm), β-Li$_3$N (P6$_3$/mmc), Li$_3$NH (Fm-3m), LiH (Fm-3m), and LiH$_2$ (I-4) were relaxed to obtain zero-temperature lattice energies of formation. Bulk free energies of formation were computed as $E_{\text{bulk}} + \text{ZPE} - T S_{\text{bulk}}$ in good agreement with previous results (see the Supporting Information and Table S2, Supporting Information, for relaxed cell parameters). Bulk free energies of formation were computed as $E_{\text{bulk}} + \text{ZPE} - T S_{\text{bulk}}$, where ZPE is the zero-point energy and $T S_{\text{bulk}}$ is the phonon contribution to the vibrational free energy, calculated within the quasiharmonic approximation (Supporting Information and Table S4, Supporting Information). To obtain effective surface energies, total cleavage energies of the low-index surfaces $s_i$ for each phase were first computed in a periodic slab geometry with 10 Å of vacuum according to $s_i = 1/2 \times (E(N) - N(E(N) - E(N-1)))$, where $E(N)$ is the energy of an $N$-layer slab, with $N$ chosen to generate slabs $\geq 1$ nm thick. The Wulff manifold was used to obtain a Wulff construction for each phase. The effective surface energy $s_f$ used in the thermodynamic calculations were computed as $s_f = A_s^{-1} \Sigma s_i q_i$, where $A_s$ is the surface area of a sphere with volume equivalent to the Wulff-constructed particle, and $q_i$ is the individual area of a facet. The free energy of H$_2$ was computed by adding finite-temperature contributions from the known equation of state to a DFT-calculated reference total energy. For surface energies and Wulff constructions, see Table S3 and Figure S5 (Supporting Information).

**Interface Energy Calculations**: Interfacial energies $\gamma_{ab}$ between phases a and b were estimated as $\gamma_{ab} = p (s_a + s_b)$, where $s$ is the effective surface energy of a phase, as an estimate of the total interaction energy. $\gamma_{ab}$ increases with decreasing $s$ and tends to zero for $s = 0$.

**Thermodynamic Phase-Fraction Calculations**: The reversible reactions $a \times [\text{LiNH}_2 + 2\text{H}_2] \iff b \times [\text{Li}_3\text{N} + \text{LiH} + \text{H}_2] \iff c \times \text{[LiNH}_2 + 2\text{LiH}]$ were considered, where $a$, $b$, and $c$ define the reaction progress. Competing reactions involving intermediate ammonia formation were not considered, since ammonia is consumed quickly upon reaction with dispersed LiH$^{18,19,34}$ (its release is also suppressed in the experimental nanocarried material; see Figure S4, Supporting Information). The Gibbs free energy $G$ is expressed as a function of temperature $T$ and H$_2$ pressure $P_H_2$ as $G(T,P_H_2) = (p_0 \times g_a) + (n_0 \times g_b)$, where $g_a$ and $g_b$ are the molar contributions for $n_a$ and $n_b$ moles of solid and gas, respectively, expressed in terms of $a$, $b$, and $c$ (Supporting Information). An ideal H$_2$ gas is assumed according to $g_{c,0} = g_{c,0}^0(T) + RT \ln (P_H_2 / P_0)$, where $g_{c,0}^0(T)$ is the reference free energy of H$_2$ gas at the standard state ($P_0 = 1$ atm).

For data in Figure 4, an ideal mixture of solid-phase fractions $X_i$ according to $g_i = g_{i,0} + \Sigma X_i g_{i,0}^0(T) + RT \ln X_i$ is also assumed (nonideal mixing is explored in the Supporting Information). The term $g_i$ includes the molar surface and interface contributions, which depend on the particle size and microstructural configuration (derivations of $g_i$ for the microstructures in Figure 1 are in the Supporting Information).
The free energies $g(T)$ of the individual pure solid components were computed from DFT, with the reference phase for Li$_3$N (eLi$_3$N vs $\beta$-Li$_3$N) chosen according to the stability crossover criterion in Figure 4a. The $X_i$ were computed by minimizing $G$ with respect to $a$, $b$, and $c$ under constraints associated with the corresponding microstructure (listed in Figure S6, Supporting Information).

All spherical core–shell geometries in Figure 1 and a rod-shaped geometry were tested to confirm robustness of the predicted size-dependent reaction pathway changes with respect to specific microstructure assumptions (Figures S6–S11, Supporting Information). The specific temperature for the isothermal plots in Figure 4 (727°C) was selected to establish a suitable reference for which well-defined stability regimes for Li$_3$N, Li$_2$NH, and LiN$_2$H$_2$ were predicted in the bulk material, and full H$_2$ desorption was achieved. This allows us to unambiguously isolate size-dependent changes to the phase transformation pathway. Results for nonideal mixing with a larger activity coefficient at 250°C are presented in Figure S12 (Supporting Information); however, since the activity coefficient introduces another unknown parameter, only ideal mixing results are presented in Figure 4 for clarity of presentation. Because pressure calibration in Figure 4c depends on temperature and does not account for nonequilibrium kinetics, attention should be drawn to the qualitative behavior of Li$_3$N phase suppression and reversibility rather than quantitative transition pressures.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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