**Supporting Information**

**Reversing the Irreversible: Thermodynamic Stabilization of Lithium Aluminum Hydride Nanoconfined Within a Nitrogen-Doped Carbon Host**

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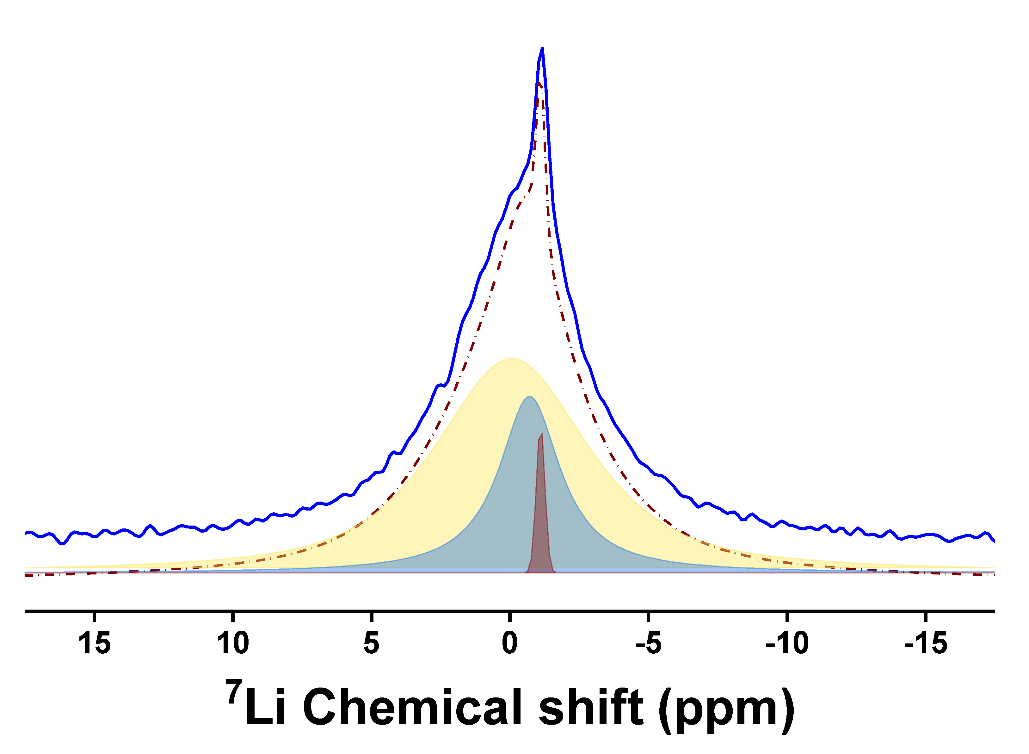
Fig. S1 Pore size distributions of a, CMK-3, LiAlH4@CMK-3; b, NCMK-3, and LiAlH4@NCMK-3.



**Fig. S2** Fourier-transformed infrared spectra (FT-IR) of CMK-3/NCMK-3 and LiAlH4@CMK-3/NCMK-3. A broad band located at 1500-1650 cm-1 was assigned to C-C axial deformation band,1,2 and an additional band at 1100-1300 cm-1 observed only for the NCMK-3 corresponds to a broad C-N stretching mode centering at 1105 cm-1.3 Two pairs of active infrared vibration bands−Al-H stretching (1760 cm-1 and 1615 cm-1) and Li-Al-H bending (900 and 830 cm-1)−were present for the recrystallized LiAlH4,4 and the equivalent bands were detected for both the LiAlH4@CMK-3 and the LiAlH4@NCMK-3 samples. No wide bands at 3000-3500 cm-1 indicating hydroxyl group were observed.



Fig. S3 PXRD patterns of a, physical mixture of LiAlH4 and NCMK-3, b, LiAlH4@CMK-3 and LiAlH4@NCMK-3 synthesized without kinetic control, and LiAlH4@NCMK-3 infiltrated by THF solution. LiCl phase is an impurity from commercial LiAlH4.5,6 The physical mixture was prepared by grinding NCMK-3 and LiAlH4 powders for 30 minutes with the same nominal loading (20 wt. %).



**Fig. S4** 7Li MAS NMR spectrum of as-synthesized LiAlH4@NCMK-3. The deconvolution components are LiAlH4 (broad blue peak and narrow red peak) and LiH (yellow peak).



Fig. S5 N 1s spectra and schematic illustration of N-functionalities (right) a, NCMK-3, LiAlH4@NCMK-3 b, and LiAlH4-treated NCMK-3. Note that LiAlH4 was washed out with the same solvent (Et2O) used for the infiltration, but the N configuration resembles that of LiAlH4@NCMK-3.

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**Fig. S6** **a,** Brightness analysis for the nanochannels present in LiAlH4@NCMK-3 **b,** HAADF-STEM line profile of LiAlH4@NCMK-3 and its corresponding EDS signal (scale bar: 50 nm).



**Fig. S7** EELS profile of Al particles (area 1, cyan filled plot) and scaffold part (area 3, red lined plot) in LiAlH4@NCMK-3. Peaks at ~15, 30, and 45 eV represent characteristic harmonic peaks of Al metal.

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**Fig. S8** Energy (in unit eV) trajectories, referenced to the energy averaged over the first 6 ps, of AIMD simulations for (LiAlH4)8 on N-free pristine graphene and pyridinic-N-doped graphene sheets. The formation of Al is spontaneous over a N-doped graphene surface; in the case of pristine graphene, the final structure from the first run of AIMD simulation was manually modified by moving four hydrogen atoms from the (LiAlH4)8 cluster to the vacuum space to mimic the reaction above with the formation of an Al atom and dihydrogen, which was continued with a separate run of AIMD simulation.

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Fig. S9 *Ex-situ* 7Li MAS NMR spectra with representative deconvolutions of the central transition 7Li MAS NMR line shapes for the non-metallic species in the a, LiAlH4@CMK-3 and b, LiAlH4@NCMK-3 samples. Recrystallized bulk LiAlH4 is shown in black. The deconvolution parameters are shown in Table S3. The deconvolution components are LiAlH4 (broad blue peak and narrow red) LiH (yellow), adsorbed LiH (pink), LiOH (green), and LiCl (dark red peak in b). LiOH and LiCl are minor impurities. Table S3 presents deconvolution details of 7Li MAS NMR.

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Fig. S10 a,** High angle annular dark field EDS map image of rehydrogenated LiAlH4@NCMK-3 and **b,** EDS spectra scanned in two area (area 1: green, area 2: red)

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**Fig. S11** Relaxed geometries of isolated Al, LiH, LiAlH4, and Li3AlH6 clusters. H, Al, and Li atoms are shown in white, gray, and purple, respectively.

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**Fig. S12** Schematic representation of spontaneous interdiffusion of (LiH)6 and Al6 cluster to form an alloyed (LiH+Al)6 phase and its energy profile. The difference in energy is normalized to one formula unit of LiH + Al.

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**Fig. S13** Coordination and formation of lithium adatoms on pyridinic nitrogen defect sites of graphene (carbon is shown in black, nitrogen in blue and lithium in purple). The Figureshows the optimized structures of graphene sheets with 4 pyridinic N defect sites before and after Li adatom formation. ∆E is the reaction energy of Li adatom formation. Here, E4Li@N-doped-graphene and EN-doped-graphene  are DFT-computed energies of the two graphene sheets shown in the figure. To obtain a ∆E value that is relevant to the reversible Li-Al-H interconversion, we use DFT-computed energies of bulk LiAlH4, Al, LiH and gas-phase H2 as corresponding references to derive ELi. Two sets of references were employed.

*i. using bulk LiAlH4, Al, and gas-phase H2 as an energy reference:*

ELi = ELiAlH4(s) – EAl(s) – 2 EH2(g)

∆E = E4Li@N-doped-graphene - EN-doped-graphene – 4 (ELiAlH4(s) – EAl(s) – 2 EH2(g))

normalized to per mole of Li adatom formation, ∆E/4 = ***-12.6*** kJ/(mol Li)

*ii. using bulk LiH and gas-phase H2 as energy reference:*

ELi = ELiH(s) – 1/2 EH2(g)

∆E = E4Li@N-doped-graphene - EN-doped-graphene – 4 (ELiH(s) – 1/2 EH2(g))

normalized to per mole of Li adatom formation, ∆E/4 = ***-22.7*** kJ/(mol Li)

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**Fig. S14** *Ex-situ* N K-edge soft TEY X-ray absorption spectra of LiAlH4@NCMK-3. The black and red lines represent simulated spectra of pristine host and Li-coordinated host.

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**Fig. S15 a,** Isosurface of charge density difference (yellow = accumulation; cyan = depletion; isosurface value 0.003 *e*) obtained by comparing a single Li atom adsorbed on a pyridinic N defect to its isolated constituents. **b**,Electronic density of states of pyridinic N-doped graphene before and after incorporation of Li adatoms.

**Table S1.** BET surface areas and total volumes of functionalized/non-functionalized scaffolds and LiAlH4 loaded scaffolds.

**Table S2.** Relative amount of nitrogen functionalities in NCMK-3 and LiAlH4@NCMK-3 samples determined by deconvolutions of N 1s XPS spectra.

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**Table S3.** NMR parameters used for deconvolution of the **a,** 27Al central transition non-metallic species and **b,** 7Li central transition line shapes. δiso is the isotropic chemical shift, lb is the line broadening, CQ is the quadrupolar coupling constant, η is the asymmetry parameter for the quadrupolar coupling constant, xG/(1-x)L is the ratio of Gaussian/Lorentzian character of the line shape, and Rel. % is the relative area of the phase. A Czjzek distribution was used for the amorphous Al2O3 deconvolution where ΔδCS denotes the full width at half maximum of the isotropic chemical shift gaussian distribution.





**Supplementary note 1.**

**Synthesis and storage of LiAlH4@NCMK-3 and LiAlH4@CMK-3**

A loading of 20wt% of LiAlH4 was achieved by infiltrating a solution of 25 mg of freshly recrystallized LiAlH4 in 1.25 mL dry diethyl ether into 100 mg of the pretreated mesoporous carbon scaffolds (CMK-3 and NCMK-3). The obtained powder samples were stored in a -30 °C refrigerator within the Ar glovebox (*Innovative Technology Inc.*).

**Supplementary note 2.**

**Identification of the origin of LiAlH4 decomposition upon solvent infiltration**

To understand the reason for LiAlH4 decomposition during synthesis, the samples were prepared under different infiltration conditions and analyzed with PXRD. First, to determine whether improved kinetics of reactions R1 and R2 in **Table 1** drives the decomposition, the effect of infiltration temperature was investigated. The original composites were synthesized at low temperature (below -50 ℃) to decelerate the reaction kinetics (“kinetic control”). Another set of nanoconfined composites were prepared without kinetic control by infiltrating the LiAlH4 solution for a prolonged time at room temperature. Both LiAlH4@CMK-3 and LiAlH4@NCMK-3 infiltrated at room temperature show some metallic Al peaks (**Fig. S6b**). Among those without kinetic control, the LiAlH4@NCMK-3 exhibits greater metallic Al intensities than LiAlH4@CMK-3, suggesting that the NCMK-3 scaffold plays a role in catalyzing the decomposition of LiAlH4.

To probe the effect of solvent on decomposition, LiAlH4 was dissolved in THF instead of diethyl ether and infiltrated into NCMK-3 to form the composite (LiAlH4@NCMK-3-THF). Interestingly, Al metallic peaks are still observed in the LiAlH4@NCMK-3-THF, even though THF is known to strongly stabilize LiAlH4 by forming a solvent adduct.7 We therefore conclude that NCMK-3 exhibits both a kinetic and thermodynamic influence on the decomposition of the loaded metal hydride.

**Supplementary note 3.**

**Detailed description of MAS NMR measurements**

All samples were handled within an Ar glovebox and packed within 2.5 mm ZrO2 rotors. To ensure stable spinning at 25 kHz, the samples were diluted by mixing with PCTFE (polychlorotrifluoroethylene) powder in a mortar and pestle. If this was not done, the free electrons inherent to carbon in CMK-3 produce eddy currents and consequently a braking torque preventing stable spinning above 10 kHz. A single pulse experiment was used for all collected 27Al spectra with a 10s recycle delay, sufficiently long enough to allow the anticipated phases (LiAlH4, Li3AlH6, and metallic Al) to fully equilibrate.8 Initially, using two-pulse phase modulation (TPPM) 1H decoupling was investigated however it was not used for acquisition as the resolution of the 27Al line shape did not improve, likely due to the high spinning speeds (25 kHz) used were sufficient to average out the 1H-27Al heteronuclear coupling. A 60° pulse length of 1.83 µs was used (radio frequency field of approximately 140 kHz) for all experiments. A larger tip angle was chosen for these measurements to maximize the signal acquisition rate, as the nanoconfined LiAlH4 in NCMK-3 makes up a fraction of the total volume and is exasperated further by the PCTFE dilution. Using these parameters, relatively high-resolution spectra were obtained by collecting data overnight (approximately 5600 scans). Additional tests using a small tip angle of 9° (pulse length of 0.275 µs) were carried out to determine how quantitative the 60° tip angle spectra were by comparison. The nutation frequency of quadrupolar nuclei like 27Al is dependent on the strength of the quadrupolar interaction, using small tip angles diminishes the nutation frequency differences leading to quantitative spectra. In the tests with 9° tip angle, the intensity of the metallic Al peak was about 1.8 times higher than that in the 60° tip angle spectra. The other non-metallic Al sites had comparable intensities between the two tip angles and because the samples contain the same Al environments across the de/rehydrogenation process, the 60° tip angle spectra can be considered semi-quantitative. Each 7Li spectra was collected using a single 60° pulse length of 2 µs (RF field of approximately 125 kHz) with a recycle delay of 60 s and is the accumulation of 32 scans. The 27Al and 7Li spectra were externally referenced to 0.1M AlCl3 (aq) solution (δiso=0 ppm) and 1M LiCL (aq) solution (δiso=0 ppm), respectively. Deconvolution of the quadrupolar 27Al MAS line shapes was carried out using the software package Dmfit.9

**Supplementary note 4.**

**Detailed description of theoretical calculations**

Plane-wave, periodic supercell DFT calculations were performed with the Vienna *ab initio* simulation package (VASP), version 5.4.4,10 using the projector augmented wave treatment of core-valence interactions11,12 with the Perdew-Burke-Ernzerhof (PBE)13 generalized gradient approximation for the exchange-correlation energy, and *van der Waals* dispersion *forces* described with D3 correction method.14A 20 Å x 20 Å x 20 Å cubic supercell was used to model isolated nanoclusters. Each structure was first sampled with 20 ps NVT *ab initio* molecular dynamics (AIMD) with the energy cutoff for a plane-wave basis set of 400 eV and the Brillouin zone sampled at the Γ-point only. Timestep was set to 1 fs and a Nose-Hoover thermostat was used to maintain the temperature at 373 K, chosen arbitrarily for annealing effect. Low-energy configurations in each trajectory were quenched to 0-K with the energy cutoff for a plane-wave basis set increased to 500 eV, self-consistent-field electronic energies converged to 10-6 eV and atomic forces to less than 0.03 eV/Å. A supercell of 6x6 graphene sheet with periodic images separated by 20 Å vacuum space (a=b=14.65 Å, c=20 Å, α= β=90o, γ=120o) was used to model interactions between carbon materials and nanoclusters of lithium(aluminum) hydride an aluminum. Structures were first annealed with AIMD at 373 K and optimized to ground states at 0 K. AIMD and geometry optimizations were performed with the nearly the same setup as for the isolated nanoclusters in vacuum except that a Γ-centered 2×2×1 k-point mesh was used to sample the Brillouin zone during geometry optimizations. Bader charge analyses were performed using the algorithm developed by Henkelman *et al*.15-17

The N K-edge X-ray absorption (XAS) spectra are calculated using the quantum espresso source code package with the Shirley reduced basis for efficient Brillouin zone sampling.18,19 Within the excited core-hole approximation20, a modified ultrasoft pseudopotential21 for N is used where a core electron is removed from its 1s core state and placed at the first available empty state above the Fermi level. Standard PBE-GGA approximation is used to approximate the exchange-correlation functional in DFT. A smooth XAS spectrum is obtained by applying a Gaussian convolution (0.2 eV width) to the calculated transition probabilities at discrete energies. Finally, the spectrum is shifted according to a previously established alignment scheme22 that uses molecular N2 as a reference.23

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