Evaluation of a new lithium complex hydride: A derivative of BH_4^- and NH^{2-} for fast Li-ion conduction and H_2 sorption

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Supporting Information

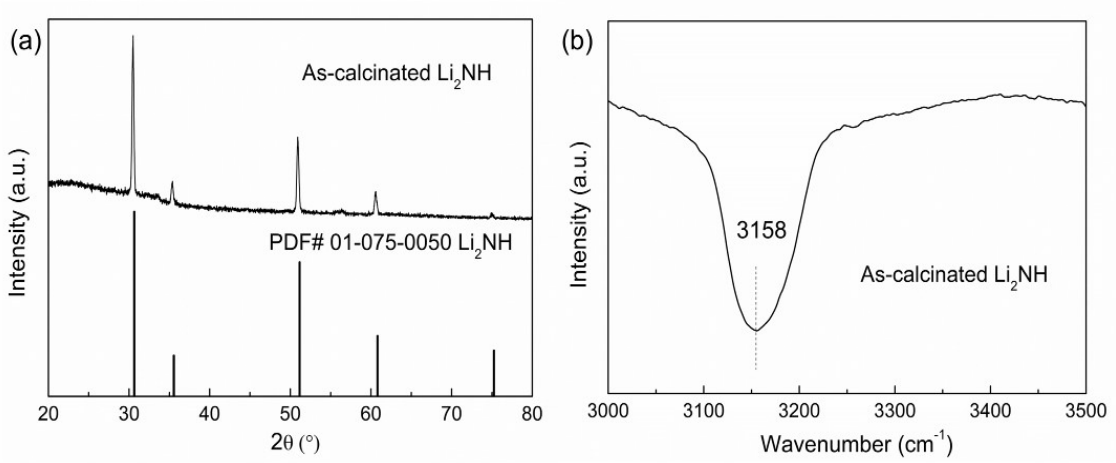

Figure S1. PXRD pattern **(a)** and FTIR spectra **(b)** of the Li_2NH sample annealed at 400 °C for 12 h.

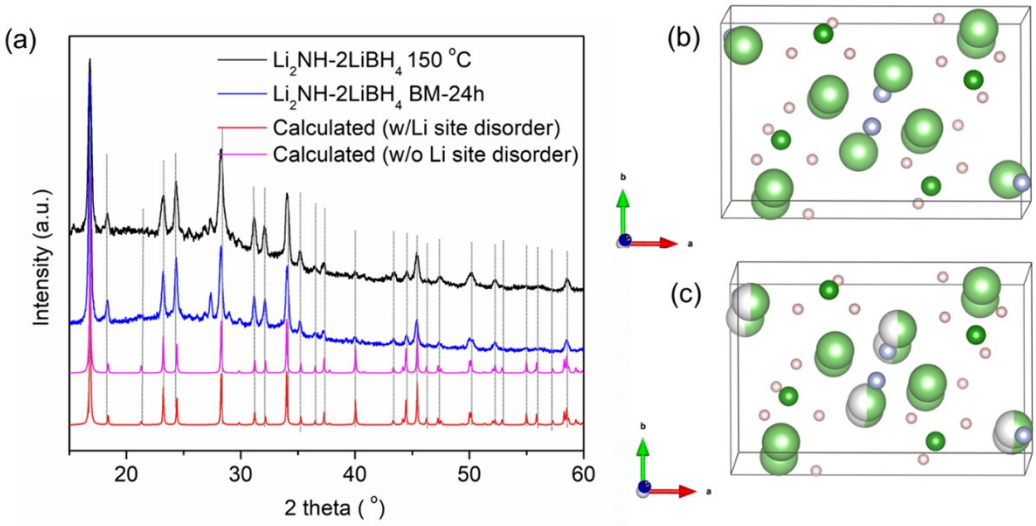

Figure S2. (a) Comparison of the observed powder XRD patterns (plotted in their absolute X-ray counts to make the distinctions visible) and the calculated pattern based on the tentative structural

model of new phase (N2). Dotted lines mark the peaks that belong to the new phase (N2). **(b)** and **(c)** are two proposed structural models for the new phase, with spatial orientation of atoms and vacancies; Li in pale green, Li/vacancies in gray-green, B in green, N in blue, and H in pink spheres.

All the samples were ball milled for 24 h according to the ratios and then heated at 150 °C for 2 h before the XRD measurement. The tentative structure model in this article was derived from the XRD pattern of Li_2NH-$LiBH_4$ with Si, which applies as an internal standard to quantify the intensity of the new phase "N2".

From the comparison of the observed and calculated XRD patterns, these two preliminary models (especially the B and N sites) may be close to the real structure. Meanwhile, the Li sites (which might also involve site disorder/partial site occupancy) were ambiguous due to the limitation of powder XRD technique to the small Li atoms. The effect of XRD scattering from Li atoms is small as it can be observed from the similarity of XRD patterns generated from these two models. Therefore, due to the uncertainty of Li sites and the possible orientational disorder of NH-, these two preliminary structure models were not used for further DFT structure optimization. At present the tentative model cannot be used as an initial input for further DFT calculations to determine the positions of H and the other missing Li and N atoms.

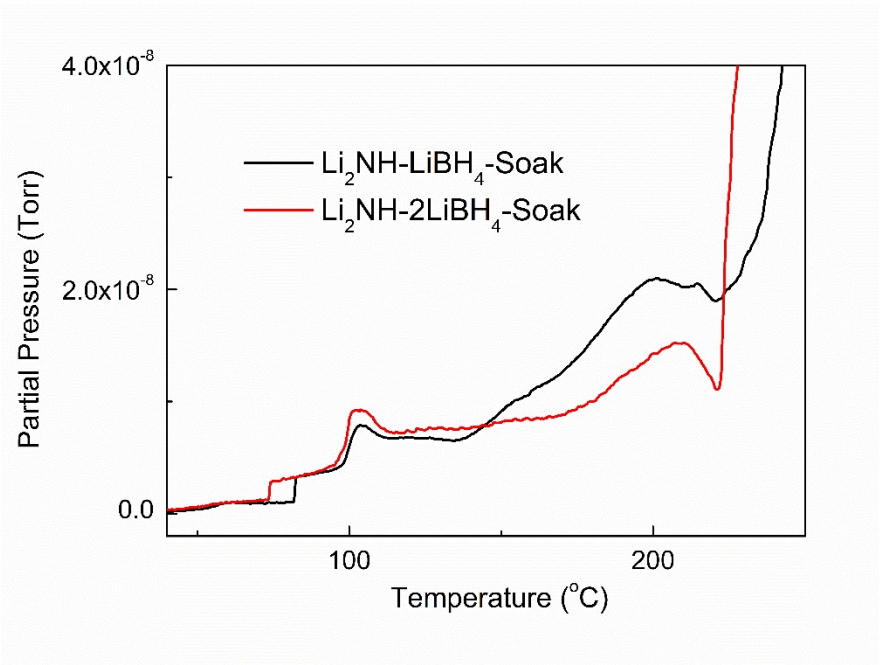

Figure S3 TPA of the Li_2NH-$xLiBH_4$ samples at 1 bar H_2 pressure of 15 ml/min.

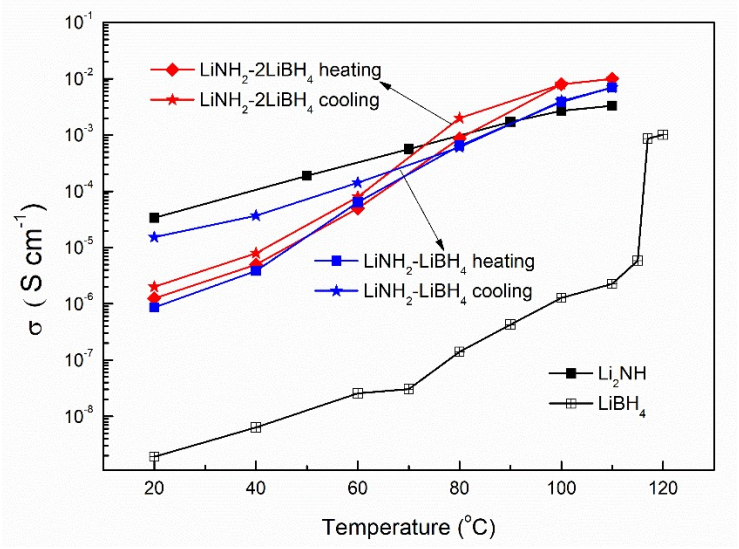

Figure S4 The hysteresis of the conductivity during heating/cooling cycles for Li_2NH-x$LiBH_4$ (x = 1 and 2) samples.

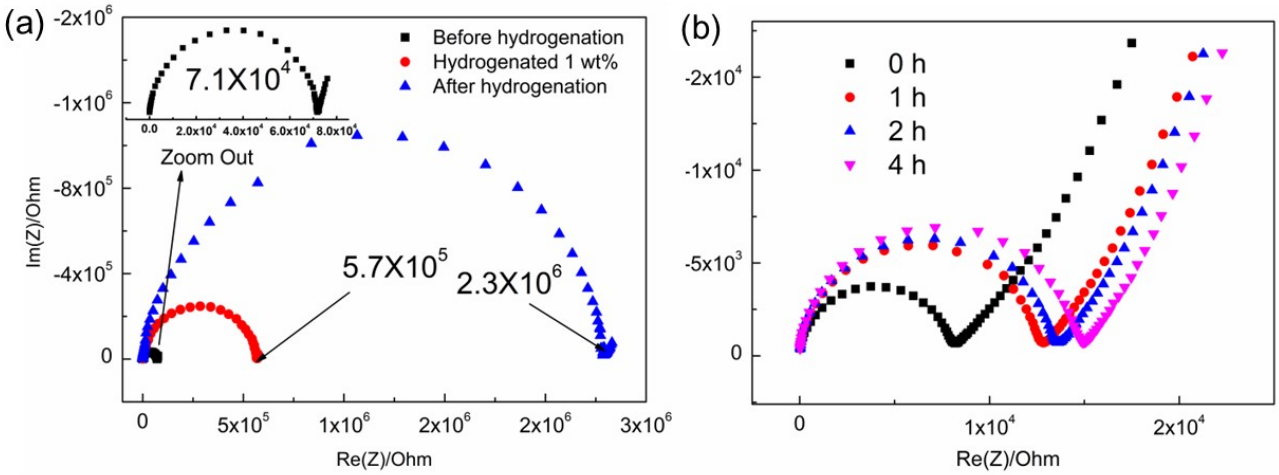

Figure S5. Impedance spectra shown on the Nyquist plot for as-prepared Li_2NH-2$LiBH_4$(N2) a) before hydrogenation, hydrogenated 1 wt% hydrogen and after hydrogenation collected at 30 °C. b) during hydrogen absorption process under 10 bar hydrogen pressure and 60 °C.