

## Supplemental Information

### Can nitrogen-based complex hydride be hydrogen isotope separation material?

Zhao ZHANG,<sup>a</sup> Hujun CAO,<sup>a\*</sup> Zhitao XIONG,<sup>a</sup> Joshua Adedeji BOLARIN,<sup>ab</sup> Weijin ZHANG,<sup>a</sup> and  
Ping CHEN<sup>ac\*</sup>

a. Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China.

b. University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

c. Collaborative Innovation Centre of Chemistry for Energy Materials (iChEM•2011), Xiamen University, Fujian 361005, P. R. China.

\*Corresponding author.

E-mail addresses: caohujun@dicp.ac.cn (H. J. CAO)

E-mail addresses: pchen@dicp.ac.cn (P. CHEN)

## Experimental details

### Materials

Lithium nitride ( $\text{Li}_3\text{N}$ ) was synthesized by nitriding metallic lithium via the following reaction:



Lithium pellet (Sigma-Aldrich, purity 99%) was used as a starting material. The product after nitrogenation was confirmed as pure  $\text{Li}_3\text{N}$  by XRD measurement (Fig S1), which consists of both  $\beta$  and  $\alpha$  phases of  $\text{Li}_3\text{N}$ . In order to evaluate the thermodynamic and kinetic isotope effects of Li-N-H system, hydrogenated samples were prepared via reactions ( $\text{Li}_3\text{N} + \text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH}$  and  $\text{Li}_2\text{NH} + \text{H}_2 \rightarrow \text{LiNH}_2 + \text{LiH}$ ). The reactions were carried out in a stainless-steel pressure vessel.  $\text{Li}_3\text{N}$  was soaked in 20 bar of  $\text{H}_2$ ,  $\text{D}_2$  and  $\text{H}_2\text{-D}_2$  mixture gases at 473 K for 10 h and subsequently ball milled for 10 h. Repeating the above steps three times to ensure the complete hydrogenation process. The  $\text{Li}_3\text{N}$  samples hydrogenated in  $\text{H}_2$ ,  $\text{D}_2$  and  $\text{H}_2\text{-D}_2$  mixture gases are simplified as Li-N-H, Li-N-D and Li-N-HD in the following text for short. The purity of gases mentioned above are higher than 99.999%.

### Measurement for isotope separation factor

The isotope separation factor was measured by single equilibration technique using a home-made apparatus. Take the Li-N-HD sample with certain deuterium concentration as starting material. The sample was heated to 473 K, 503 K, 543 K and preserved for 3 hours, respectively. The equilibrium released gas of Li-N-HD sample was collected for MS measurements. The MS signals of  $\text{H}_2$  and  $\text{D}_2$  are calibrated using linear fitting. Several  $\text{H}_2\text{-D}_2$  mixtures with certain molar ratio were prepared and analyzed by MS for quantitatively measuring the responsive intensities of isotopes in MS corresponding to their molar ratio. The responsible intensity of hydrogen isotope in MS and its molar ratio is summarized in table 1.

Table 1. The responsible intensity of hydrogen isotope in MS and its molar ratio

Intensity ratio ( $\text{D}_2/\text{H}_2$ )	Molar ratio ( $\text{D}_2/\text{H}_2$ )
0.067	0.267
0.179	0.662
0.27	1
0.498	1.819

0.875

3.112

By plotting the above data for fitting (shown in Fig. S3), the relationship of responsible intensity of hydrogen isotope in MS and its molar ratio is derived, which is used for calculating D/H on the base of MS results. The average of H<sub>2</sub> and D<sub>2</sub> was used as the calibration value for HD since HD gas is not commercially available.

According to the single equilibration technique, the home-made apparatus is comprised of a reactor, mixture gas resource, pressure manometer and mass spectrometer equipped with vacuum system which has been illustrated in Fig. S4. [1] The volume of each chamber has been calibrated in advance.

The hydrogen isotope separation factor was calculated by the following equation, where ([D]/[H])<sub>gas</sub> and ([D]/[H])<sub>solid</sub> are the ratio of deuterium to hydrogen in gas phase and solid phase, respectively.

$$\alpha_{H=}^D = \frac{([D]/[H])_{\text{gas}}}{([D]/[H])_{\text{solid}}} \quad (\text{R2})$$

A certain amount of H<sub>2</sub>-D<sub>2</sub> gas mixture was introduced into the reactor at different temperature such as 453K for hydrogenating Li<sub>3</sub>N. Thus, the [D]/[H] solid could be derived on the base of pressure and MS data collected during hydrogenation. Subsequently, the isotope separation measurements of Li-N-H system were carried out at different temperature. The release gas from reactor is the [D]/[H] gas which could be directly analyzed by MS.

#### ***Measurements for pressure-concentration isotherm (PCI)***

Pressure-concentration isotherm (PCI) measurements were carried out by a home-made Sievert-type apparatus for evaluating the thermodynamic property of Li-N-H/Li-N-D system. The original experimental data such as temperature and pressure were monitored and recorded automatically by computer. The exact volume of each part containing reservoir had been carefully calibrated. The hydrogen released during desorption could be calculated by using equation R3, where P is the equilibrium pressure, V is the volume of reactor, n is the molar of sample, R is thermodynamic constant (8.314) and T is temperature.

$$PV=nRT \quad (\text{R3})$$

The PCI desorption tests were performed at 548 K, 558 K and 593 K for Li-N-H and Li-N-D samples.

According to van't Hoff equation (R4), where P is desorption equilibrium pressure, R is thermodynamic constant and T is temperature.

$$\ln\left(\frac{P}{P^\ominus}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (\text{R4})$$

The logarithm of the plateau pressure versus the reciprocal of the absolute temperature could yield a straight line, from which the enthalpy and entropy could be calculated.

### ***Measurements for desorption kinetics***

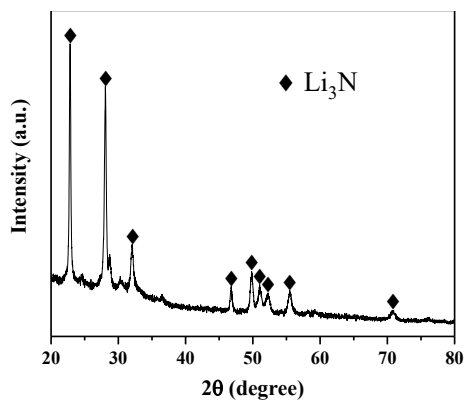
The kinetic isotope effects were characterized using a home-made temperature programmed desorption system which is equipped with a mass spectrometer (HPR20, Hiden) (TPD-MS). The heating rate was controlled as 2, 4, 6, 8 K/min. Using Kissinger's method (R5), where  $T_p$  is the peak temperature of desorption,  $\beta$  is heating rate,  $E_a$  is activation energy and R is thermodynamic constant.

$$d[\ln(\beta/T_p^2)/d(1/T_p)] = -E_a/R \quad (\text{R5})$$

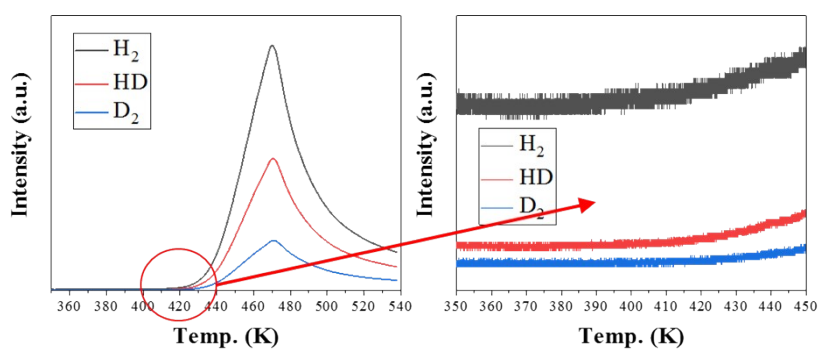
The activation energy  $E_a$  can be calculated from the slope of  $\ln(\beta/T_p^2)$  versus  $1/T_p$ .

### ***Characterizations***

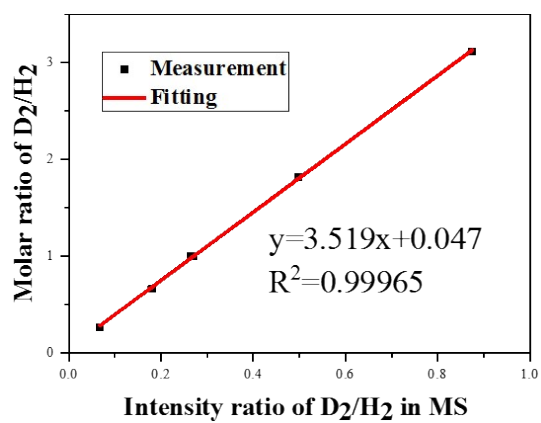
Powder X-ray diffraction (XRD) measurements were conducted using an X'Pert Pro diffractometer with Cu K $\alpha$  radiation at 40 kV and 40 mA. Fourier Transform Infrared (FT-IR) spectra were recorded using a Bruker Tensor II under a diffuse reflectance infrared Fourier transform (DRIFT) mode. In order to monitor the transformation of nitrogen-based species during H/D exchange process, an air-tight in-situ reactor was designed for FT-IR measurement. The spectra were recorded in a range of 4000-400  $\text{cm}^{-1}$  at elevated temperature and H/D gas atmosphere with 32 scans and a resolution of 4  $\text{cm}^{-1}$ . For avoiding oxidation of the sample, before the XRD measurements, all powders were loaded in an air-tight sample holder equipped with a foil hood and then sealed in the glovebox.



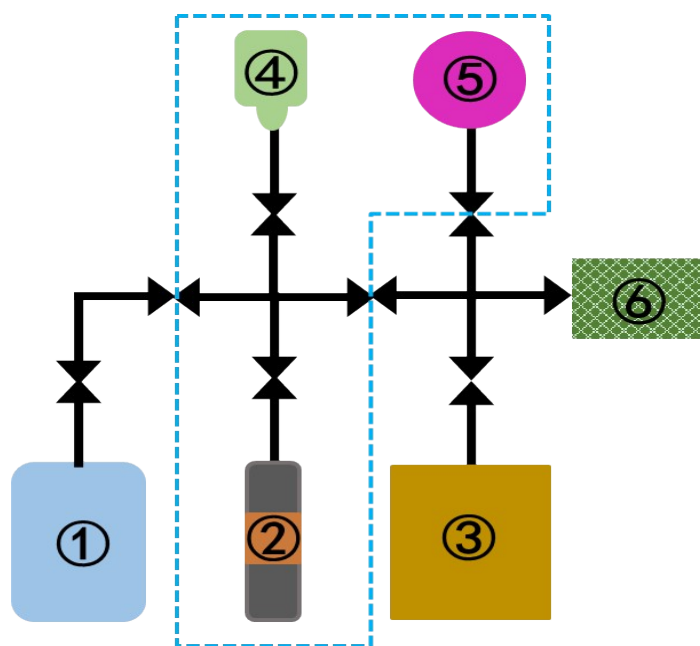
**Fig. S1.** XRD of as-synthesized  $\text{Li}_3\text{N}$ .



**Fig. S2.** TPD curve of Li-N-HD sample and the enlarged curve of starting point.



**Fig. S3.** Fitting curve of intensity of hydrogen isotope in MS versus its molar ratio.



**Fig. S4.** Illustration of home-made apparatus for measuring hydrogen isotope factor

(① Mixture gas resource, ② Reactor, ③ Mass spectrometer, ④ Reservoir, ⑤ Pressure manometer, ⑥ Vacuum pump ).

#### Reference

[1] Y. Yang, D. Luo, W. Guo, et al. *J. Phys. Chem. C*, 2015, **119**, 3481-3487.