Effect of lithium ion conduction on hydrogen desorption of LiNH₂-LiH solid composite

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Experiment details

The powder of $LiNH_2$ (95 %), LiH (95 %), $LiCO_3$ (99.997 %), TiO_2 (99 %), and Ti_2O_3 (99.9 %) were purchased from Sigma-Aldrich. $LiTi_2O_4$ was synthesized through a two-step solid-solid reaction. $Li_2Ti_2O_5$ will form as an intermediate compound [1]. See Equations (3) and (4):

$$Li_2CO_3 + 2TiO_2 \rightarrow Li_2Ti_2O_5 + CO_2 \qquad (3)$$

$$Li_2Ti_2O_5 + Ti_2O_3 \rightarrow 2LiTi_2O_4 \qquad (4)$$

$LiTi_2O_4$ was prepared according to the procedure stated by Xu et al. [1, 2]. A 0.15 molar excess of Li_2CO_3 was added in Equation (3) to give $LiTi_2O_4$ due to the volatility of Li. An additional factor is the sensitivity of $LiTi_2O_4$ to air. This issue was outlined by several groups [3-5], regardless of the preparation method used. The aging reaction is the topotactic oxidation of $LiTi_2O_4$. $LiTi_2O_4$ reacts with oxygen or H_2O in air and is progressively transformed into $Li_{1-x}Ti_2O_4$ (0 ≤ x≤ 0.8). The polycrystalline sample is stored in an Ar atmosphere in order to avoid the aging reaction.

Commonly, a ball-milling equipment (Fritsch P7) was used to ensure a homogeneous mixing between the starting materials and the additive. $LiNH_2$ and LiH powders of 300 mg with 1: 1.2 molar ratio and 0.5 mol % $LiTi_2O_4$ were milled for 2 h. In the high energy ball-milling process, powder and 20 steel balls (SUJ-2) with a diameter of 7 mm were brought into a Cr steel pot (SKD-11) and milled at 400 rpm for 2 h under a hydrogen gas (99.9999 % purity) pressure of 1 MPa at room temperature. The ball-to-powder ratio was 100:1. The milling was interrupted every 1 h for 30 min in order to prevent frictional heat during the milling process.

After ball-milling, the mixtures were analyzed by Thermo gravimetry and differential thermal analysis (TG-DTA) equipment (HITACHI BRUKER TAPS3000S) combined with Thermal gas desorption mass spectrometry (TDMS) upon heating up to 673 K with a heating rate of 5 K/min. TG-DTA equipment was installed in another glove box to avoid exposing the sample to air in their measurements. Hydrogenation process was set at 473 K under 1 MPa H_2 pressure. Furthermore, structure properties were examined by XRD measurement.

The electrical conductivity was measured by ac complex impedance method by a Solartron SI-1260 impedance analyzer in a frequency range from 1 Hz to 10 MHz under the control of a PC. The sample disks (8 mm in diameter and ca. 1.5 mm in thickness) formed by pressing the powdered material were sandwiched between lithium-metal electrode and set in a 2-electrode cell in the glove box filled with purified argon. The cell was placed in a

thermostatic oil bath in order to control the temperature. Temperature ranges for the measurement were from RT to above and below reaction temperatures for $LiNH_2$ and LiH mixture. The observed impedance data were analyzed as a conventional method for evaluating the electrical conductivity from the diameter of a single arc observed on the impedance plot.

Other supporting results

The ionic conduction results of $LiTi_2O_4$ respectively doping into LiH, $LiNH_2$ (as shown in the following), and the mixture of them (the Fig. 2 in manuscript) indicate that these Li compounds as well as their mixture inherently have lithium ionic conductivity, which are enhanced by $LiTi_2O_4$ addition. The enhancement should be due to the improvement of Li^+ mobility of the compounds rather than the increase of Li^+ number from the additive $LiTi_2O_4$ added only with 0.5 mol%.
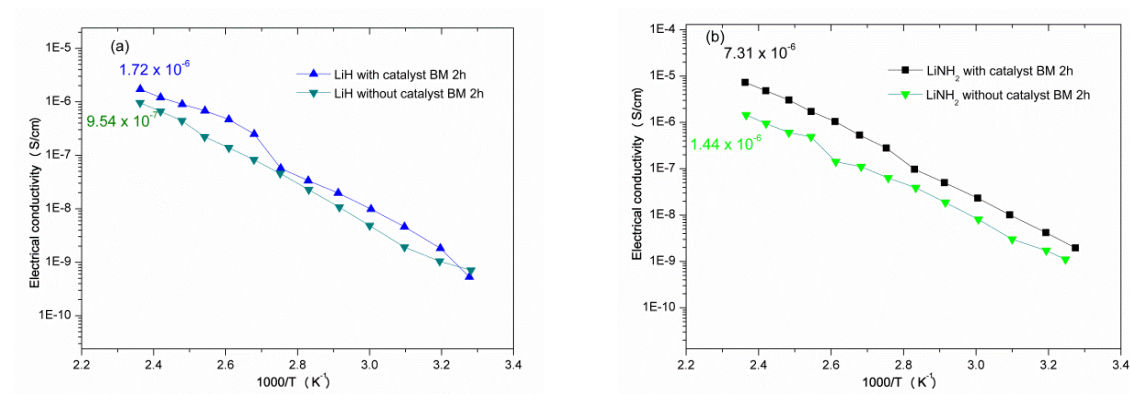

Figure S1. Arrhenius plots of the electrical conductivities for LiH and $LiNH_2$ with/without catalyst, separately.

In practice, the dwell time of impedance measurement at each temperature is automatically determined for ensuring the accuracy and reproducibility, and is usually between 90 min and 120 min at each temperature. In this case, the mixture sample at 423 K consists of $LiNH_2$, LiH and Li_2NH with/without catalyst. Alternatively, we did the isothermal hydrogen-release test of the two samples at 423 K and considered the results should be helpful for clarifying the component of the mixture samples. The measurement is performed using a heating rate 20K/min to rapidly heat the sample up to 423K and then keep for 120 min. The results shown in the Figure S2 below indicate that the catalyzed sample is undergoing dehydrogenation at 423K and almost reaches to the extent of reaction 0.35 after kept for 120 min, whereas the reference sample almost remains irresponsive during the whole process.
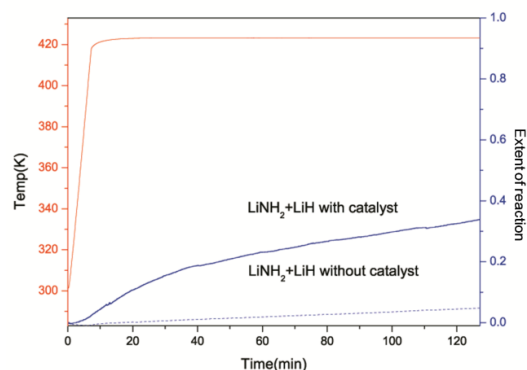

Figure S2. The isothermal hydrogen-release test of the two samples at 423 K.

In order to clarify the catalytic effect on hydrogenation process, the reversibility properties of the reaction and the hydrogenation rate have been investigated. A series of experiments have been done to examine the addition effect on hydrogen absorption of the mixture with $LiTi_2O_4$ additive. After dehydrogenation, the samples with/without $LiTi_2O_4$ addition were hydrogenated at the same temperature and hydrogen pressure for 10 min, 100

min, and 200 min, respectively. Figure S3 shows the corresponding hydrogen-uptake amount for samples with/without catalyst after 200 min-hydrogenated. The results of hydrogen pressure change during hydrogenation process are shown in the following Figure S4. The hydrogenation rate of the sample with $LiTi_2O_4$ addition is obviously higher than that of the reference sample by 3.5 times for 10 min, 1.9 times for 100 min, and 1.7 times for 200 min hydrogenation, respectively (Table S1). Furthermore, the durability of the catalytic effect of $LiTi_2O_4$ was examined by 10-cycle test (Figure S5). From these results, it is evident that the catalyst not only had effect on dehydrogenation process, but also on the hydrogenation process.
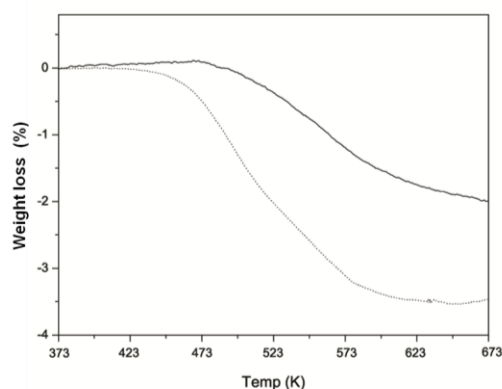

Figure S3. Corresponding weight loss of re-hydrogenated samples: $LiNH_2$ + LiH mixture hydrogenated for 200 min (solid line); $LiNH_2$ + LiH + 0.5 mol% $LiTi_2O_4$ mixture hydrogenated for 200 min (dash line).
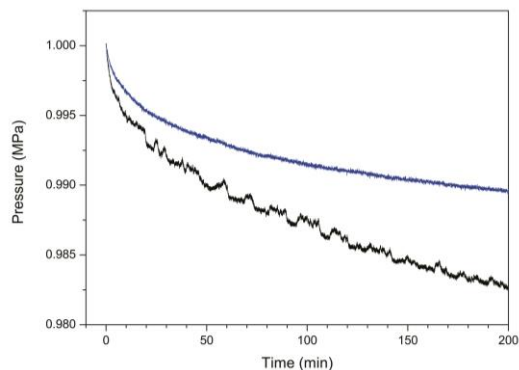

Figure S4. Hydrogen pressure change during hydrogenation process: $LiNH_2$ + LiH mixture (40 mg) hydrogenated for 200 min (blue line); $LiNH_2$ + LiH + 0.5 mol% $LiTi_2O_4$ mixture (40 mg) hydrogenated for 200 min (black line).

Temperature and Pressure		473 K, 1 MPa H_2		
Hydrogenation Time (min)		10	100	200
Hydrogenation Rate (%)	w/o catalyst	9	23	34
	w/ catalyst	32	44	60

Table S1. The catalytic effect of hydrogenation is showed from the hydrogenation ratio.
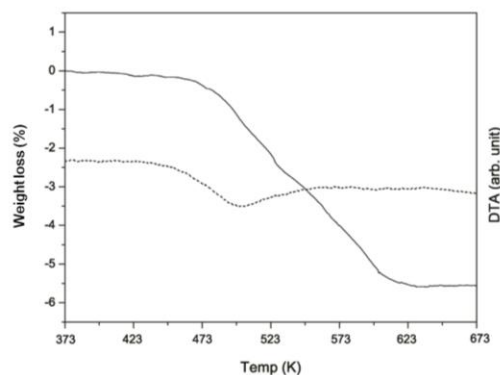
Figure S5. Corresponding weight loss of $LiNH_2$ + LiH + 0.5 mol% $LiTi_2O_4$ mixture de/hydrogenated for 10-cycle(solid line) and differential thermal analysis(dash line).

The appropriate amount of $LiTi_2O_4$ in the system was illustrated by doping different amounts of $LiTi_2O_4$ into the mixture. The DTA curves and peak temperature for a 0.5 mol% sample was the same as that of a 2 mol% sample. These results indicate that there is no simple relationship between the catalytic effect and the amount of catalyst(Figure S6).[6]
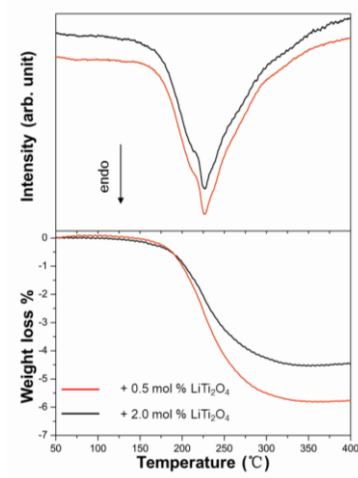

Figure S6. Corresponding weight loss of $LiNH_2$ + LiH mixture milled for 2 h with different amounts of $LiTi_2O_4$ and differential thermal analysis. Reprinted from Ref [6].

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