X-RAY DIFFRACTION STUDIES OF LI-BASED COMPLEX HYDRIDES AFTER PRESSURE CYCLING

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ABSTRACT

X-ray diffraction studies have been performed on Li-based complex hydrides after multiple hydriding/dehydriding pressure cycles. The effects of pressure cycling are important for long-term reliability of Li-based hydrides. Commercial grade hydrogen containing low-level impurities (O₂, H₂O, CO/CO₂) was used for this study to show the effect of cycling on hydrogen storage capacities. Equilibrium isotherms were obtained using a Sievert’s apparatus after 1, 56, 163, 500, and 1100 pressure cycles on the Li₂NH-LiNH₂ system to observe hydrogen capacity as a function of cycles at 255 °C. Structural studies of the products (desorbed condition) after pressure cycling showed mainly Li₂NH and LiH phases and the impurity Li₂O phase. Quantitative X-ray diffraction calculations showed the Li₂NH phase was reduced from 79% to 13%, and the LiH phase increased from 8% to 54% after 1100 cycles. Pressure cycling results showed 2.55 wt% (~10.25 bar) and 2.9 wt% (~0.86 bar) hydrogen storage loss after 1100 cycles. Detailed results of structural behaviors and pressure-composition isotherms after multiple cycles are also presented.

INTRODUCTION

Light metal complex hydrides show there is a potential for hydrogen storage using hydrides in fuel cell, on-board vehicular, and other applications [1]. Recent research found that Li-based hydrides are candidates for reversible hydrogen storage [2–5]. Lithium nitride (Li₃N) has a theoretical capacity of up to ~11 wt% hydrogen when fully converted to LiNH₂. Li₃N will absorb up to 11.5 wt% hydrogen with a reversible capacity of 7 wt% [6,7]. Eq. (1) shows the reaction for full conversion of Li₃N to LiNH₂, and Eq. (2) shows the proposed reversible reaction:

\[
\text{Li}_3\text{N} + 2\text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + 2\text{LiH}
\]

\[
\text{Li}_2\text{NH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + \text{LiH}
\]

The effect of different types of Ti catalysts in Li-N-H hydrogen storage systems are reported [2,3]. Other research has shown improvement of the reversible hydrogen storage properties by mixing different ratios of LiNH₂/LiH [8] and LiNH₂/Li₃N [9]. Structural studies and in situ deuteration/dedeuteration structural studies of Li₃N using powder neutron diffraction were performed recently [10,11]. Phase transformation behaviors of Li₂ND, LiD, and LiND₂ phases during hydriding/dehydriding of Li₃N are also reported [12].

The commercial Li₃N used was a two-phase mixture of α-Li₃N and β-Li₃N. The structure of α-phase is hexagonal with \textit{P}6/mmm space group and lattice constants \(a = 3.648(1) \ \text{Å} \) and \(c = 3.875(1) \ \text{Å} \) \((Z = 1)\) [13,14]. The β-phase is a high-pressure phase and has a hexagonal structure in
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the \textit{P6}_3/mmc space group with \(a = 3.552(1)\) Å and \(c = 6.311(3)\) Å \((Z = 2)\) [15]. Detailed low-
temperature neutron powder diffraction structural behavior studies of \(\alpha\)-Li\(_3\)N and \(\beta\)-Li\(_3\)N phase have been performed [10,16]. The structure of Li\(_3\)NH was reported as cubic (\textit{Fm}-3\textit{m}) with \(a = 5.0742(2)\) Å using synchrotron X-ray diffraction [17] and neutron powder diffraction [18]. The crystal structure of LiNH\(_2\) was determined by Juza \textit{et al.} [19] and re-determined by Jacobs \textit{et al.} (single-crystal X-ray diffraction) [20], and also determined by Miwa \textit{et al.} [21] and Yang \textit{et al.} by neutron powder diffraction [22] as tetragonal with \(a = 5.03442\) and \(c = 10.25558\) Å (space group \textit{I}-4). However, understanding the behavior of long-term hydrogen storage properties is important. In this paper, long-term pressure cycling effects using hydrogen gas containing low-
level impurities (O\(_2\), H\(_2\)O, CO/CO\(_2\)) on Li-based complex hydrides are presented.

EXPERIMENTAL

The Li\(_3\)N powder sample (80 mesh) was obtained from Sigma-Aldrich and stored under argon atmosphere. Samples were loaded inside the glove-box with argon gas. The loaded Li\(_3\)N samples were heated to 250 °C under vacuum for 4 h to remove the \(\beta\)-Li\(_3\)N phase before cycling tests. Pressure cycling experiments were performed by using “Pressure Cycling Apparatus” at the University of Nevada, Reno (UNR). The hydrogen gas used in this study was commercial grade hydrogen containing low-level impurities (O\(_2\) = 0.39 ppm, H\(_2\)O = 22.9 ppm, hydrocarbon < 0.01 ppm, and CO+CO\(_2\) < 0.10 ppm). The loading and unloading hydrogen pressure cycle was performed every hour. Equilibrium pressure isotherms were obtained by using the Sievert’s reactor at UNR and used to measure the hydrogen storage capacities. The Sievert’s reactor is automated using National Instruments automation equipment and LabView software. The operation temperature for all cycling and equilibrium isotherms was 255 °C. The phase identification and structural behavior analysis of all cycled samples (desorption) were determined using a PANalytical X’Pert PRO X-ray diffraction system. The X-ray diffraction data were analyzed by PANalytical X’Pert HighScore Plus software.

RESULTS AND DISCUSSION

The isotherm of Li\(_3\)N obtained from Sievert’s reactor is shown in Figure 1(a), which is similar to that obtained by Chen \textit{et al.} [6]. The hydrogen absorption capacity was \(\sim 10.07\) wt% at 10.25 bar gas pressure and \(8.55\) wt% at 0.89 bar gas pressure. This result confirmed Reaction (1). Chen \textit{et al.} [6] reported \(\sim 10\) wt% of hydrogen absorption capacity at 255 °C. For the desorption curve, 9.10 wt% of hydrogen was observed at 0.70 bar gas pressure. The fully dehydried Li\(_3\)N sample was examined with X-ray diffraction, and the XRD pattern is shown in Figure 1(b). The major phases were identified as Li\(_2\)NH and LiH. The phase wt% of Li\(_2\)NH and LiH are \(79\) wt% and \(18\) wt%, respectively. The impurity phase of Li\(_2\)O phase (5 wt%) was also found as seen in Figure 1(b). This result shows that the LiNH\(_2\) phase [final product of Reaction (1)] completely transforms to Li\(_2\)NH after desorption.
Figure 1. (a) The “0-cycle” equilibrium pressure isotherm of Li$_3$N shows the high hydrogen absorption capacity. (b) XRD pattern of the completely dehydrided “0-cycle” Li$_3$N sample shows mainly Li$_2$NH and LiH phase and a small amount of the Li$_2$O impurity phase.

After the first pressure cycle, cycling tests were performed. The equilibrium pressure isotherms were obtained after 1, 56, 163, 501, and 1100 cycles. The absorption isotherms for 1, 56, 163, 501, and 1100 cycles are shown in Figure 2. The 1-cycle absorption curve shows that 5.89 wt% of hydrogen absorption capacity at ~10.25 bar gas pressure and 4.27 wt% at ~0.86 bar as the starting materials are Li$_2$NH and LiH [based on the XRD result in Figure 1(b)], rather than the Li$_3$N in the “0-cycle” run. The result is close to the theoretical value of 7 wt% hydrogen absorption capacity in Reaction (2). The effects of impurity on hydrogen capacity after cycling can be observed in Figure 2. The hydrogen capacity decreases as the number of cycles increase. Pressure cycling results showed that there is 2.55 wt% (@~10.25 bar) and 2.9 wt% (@~0.86 bar) hydrogen loss after 1100 cycles. The losses after 1, 56, 163, 501, and 1100 cycles are listed in Table I.

<table>
<thead>
<tr>
<th>Number of cycles</th>
<th>∆ wt% hydrogen loss (based on maximum capacity @~10.25 bar)</th>
<th>∆ wt% hydrogen loss (using isotherm maximum plateau @~0.86 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>56</td>
<td>0.9</td>
<td>0.55</td>
</tr>
<tr>
<td>163</td>
<td>1.4</td>
<td>1</td>
</tr>
<tr>
<td>501</td>
<td>2.9</td>
<td>2.6</td>
</tr>
<tr>
<td>1100</td>
<td>2.55</td>
<td>2.9</td>
</tr>
</tbody>
</table>

X-ray diffraction analyses of the products after cycling with impure hydrogen gases and subsequently obtaining the equilibrium isotherms are shown in Figure 3. The 1-cycle diffraction pattern indicates formation of imide and other products. The cycled products after 56, 163, 501, and 1100 are also shown in Figure 3. The quantitative phase analyses of the different pressure cycles are shown in Figure 4. The phase in desorbed condition showed mainly Li$_2$NH, LiH, and Li$_2$O phases. The XRD pattern showed nearly complete reversal from LiNH$_2$ → Li$_2$NH after cycling with the expected LiH phase and Li$_2$O impurity phases. After 1100 pressure cycles, the LiH phase increases from 8 to 54 wt%, and the Li$_2$NH phase decreases from 79 to 13 wt%. The decrease in amount of Li$_2$NH can be observed in the Bragg peak at 30.5° of the XRD patterns in...
Figure 3. The impurity Li$_2$O phase was increased from 6 to 28 wt% after 1100 cycles. The increase in the amount of Li$_2$O is indicated by the increase in Bragg peak intensity at 56°. We believe that the decrease is a result of impurities present in the commercial hydrogen gas, even at the low concentration (ppm level) presented in the system. A very small amount of LiOH phase was also found in the XRD results. The amount of the LiOH phase did not show a significant change after 1100 cycles.

Figure 2. Absorption pressure isotherms of 1, 56, 163, 501, and 1100 cycles show loss of ~2.53 wt% hydrogen at ~12 bar gas pressure after 1100 cycles for the imide/amide system.

Figure 3. X-ray diffraction analyses of 1, 56, 163, 501, and 1100 cycles. The increased amount of the Li$_2$O is indicated by the increase in Bragg peak intensity at 56° and decrease in the amount of Li$_2$NH at 30.5°.
SUMMARY

Non-equilibrium pressure cycling tests and equilibrium isotherms have been obtained for different number of cycles. Absorption pressure isotherms showed that the hydrogen absorption capacity decreases as the number of pressure cycles increase. XRD patterns showed nearly complete reversal from LiNH₂ → Li₂NH after cycling, and LiH as well as impurity phases (Li₂O and LiOH) are presented in the system. Quantitative X-ray diffraction results showed formation of Li₂O impurity Li₂O phase of up to 28 wt% after 1100 cycles with commercial hydrogen. In addition, the Li₂NH was reduced from 79 to 13 wt% with concurrent increases in LiH from 8 to 54 wt% after 1100 cycles.

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REFERENCES