Study on Metal Hydride Performance for Purification and Storage of Bio-H₂

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Biomass-derived hydrogen (Bio-H₂) has been attracting much attention as a low environmental load type of hydrogen. Among the potential applications of Bio-H₂, use as a fuel for polymer electrolyte membrane fuel cells (PEMFCs) would require the removal of contaminants. Therefore, we propose the use of metal hydride for the purification and storage of Bio-H₂. Metal hydride can store a larger volumetric amount of hydrogen than that under high-pressure or liquefied, and the hydrogenate is processed at near atmospheric pressure and room temperature. In addition, by exploiting the selective hydrogen absorption properties of metal hydride, we have successfully reduced the concentration of methane as well as carbon monoxide and carbon dioxide in the hydrogen using a lanthanum-rich mischmetal alloy, the storage performance of which was evaluated in our previous study. Pressure swing adsorption was used to reduce the contaminant concentration, which was measured as 3% methane. For practical application, the influence of methane on the hydrogen absorption performance of the metal hydride is examined and the hydrogen recovery rate over the hydrogen absorption and desorption processes is evaluated.

Key Words
Metal hydride, Purification, Hydrogen storage, Bio-H₂

1. Introduction

Biomass, which includes agricultural and livestock waste, can be used to produce fuel and has been focused on as a clean distributed energy source. Biomass-derived hydrogen (Bio-H₃), which is produced using a gasification process, has potential for use as a fuel for fuel cells. Considering the application of Bio-H₂ to polymer electrolyte membrane fuel cells (PEMFCs), which supply electrical power for small to middle range applications such as fuel cell vehicles and portable devices, the removal of contaminants in Bio-H₂ is a critical issue. Bio-H₂ contains carbon monoxide, carbon oxide, methane, and other contaminants, depending on the feedstock. As such, a 2-step pressure swing adsorption (PSA) process with appropriate absorbents has recently been successfully improved to provide higher hydrogen purity. A life-cycle assessment has also been performed to evaluate the energy consumption of this operation. Using synthesis gas, all contaminants except for 3% of methane was removed at an operation pressure of 0.4 MPaG. Further purification of Bio-H₂ is required to achieve...
longer lifetime and higher efficiency of PEMFCs. PEMFCs generally operate at the stoichiometric ratio near 1.0 for hydrogen to minimize fuel loss, which means almost all hydrogen is consumed in the anode, unlike oxygen in the cathode. If hydrogen supplied to the anode contains impurities, even at small concentrations, and the PEMFC is operated in dead-ended mode, then the impurities are condensed and the decreased hydrogen partial pressure results in significant deterioration of performance. For a PEMFC system with a circulation pump at the anode, frequent hydrogen purging is required to remove the impurities, which leads to a lower hydrogen utilization ratio. However, further purification with a PSA system requires gas pressures higher than 0.4 MPaG and additional electrical power for pressurization.

We have proposed the use of metal hydride to purify and store Bio-H2 in a single process. Metal hydride can store approximately one thousand times the amount of hydrogen of its own volume, and by exploiting the selective hydrogen absorption properties of the metal hydride, the contaminant concentrations can be decreased. Fig. 1 shows the mechanism for hydrogen purification using a metal hydride. Hydrogen and impurity gases (methane in this case) are supplied to the container. Metal hydride absorbs the hydrogen and the impurity is still present as a gas phase. During the gas release process from the metal hydride, the impurity gas is exhausted first, and then the hydrogen. If the equilibrium pressure can be controlled to correspond to the output gas pressure of the PSA, then no extra power is consumed to store and purify the hydrogen, and the efficiency of the entire system can be improved.

There have been various attempts to remove contaminants in hydrogen using metal hydride. The removal of carbon monoxide is a particular challenge because it strongly poisons the metal hydride surface. Taniguchi et al. have demonstrated that high concentrations of carbon monoxide are removed with metal hydride at temperatures higher than 120 °C without poisoning. Borozone et al. performed a kinetic study on metal hydride with carbon monoxide, which showed that carbon monoxide only has an influence on the absorption rate. Contaminant removal systems using metal hydride have been proposed to date: Boyano et al. combined a steam reformer with metal hydride; Miura et al. developed a system with a carbon monoxide adsorbent and attained a hydrogen recovery ratio of 83% and the recovery ratio was also improved to 94% by blending iron powder with AB5-type metal hydride. Fluorination treatment improves durability against poisoning. Taniguchi and Ishida reported that fluorination-treated metal hydride suffered no poisoning, even for carbon monoxide concentrations as high as 100 ppm.

The structure of metal hydride is a strong factor in its durability and purification performance. ABS-type metal hydride that includes LaNi5 is durable in carbon dioxide, which typically poisons various types of metal hydrides. The influence of AB sites and additive metals on the durability against carbon dioxide poisoning has been investigated, and the cycle life of hydrogen absorption/desorption has also been tested.

Metal hydride containers have also been developed for vehicle use. Metal hydride has poor heat conduction and releases heat during hydration; therefore, container design is important to remove heat generated during the hydration process and to accelerate the hydration rate. In the future work, we are planning to develop a metal hydride cartridge that is appropriate for mobile electronic devices.

However, to our knowledge there have been no detailed reports that deal with the removal of high concentrations of methane in hydrogen using metal hydride; therefore, the hydrogen absorption and desorption performance of metal hydride requires evaluation. In this study, the influence of methane on the amount of hydrogen absorption on metal hydride is examined and the hydrogen purification performance during the hydrogen absorption and desorption process is evaluated.

2. Experimental

The gas obtained from a PSA system consists of 3% methane and 97% hydrogen. Instead of using the actual gas from a PSA system, a simulated gas mixture of pure hydrogen and methane was utilized. In this study, a lanthanum-rich mischmetal alloy was employed because
The lanthanum-type alloy has higher durability against impurities than other alloys, and use of a mischmetal enables the refining cost to be reduced with respect to that with pure lanthanum.

Fig. 2 and Fig. 3 show a schematic diagram and a photograph of the experimental setup, respectively. The simulated gas was stored in advance in a buffering cylinder. Pure hydrogen and methane were mixed in the buffer cylinder. The amount of hydrogen and methane were respectively measured with a pressure sensor attached to the buffering cylinder. The resultant gas was held overnight and then analyzed using a gas chromatograph with a Shincarbon ST column 60 sccm of hydrogen as a carrier gas to confirm the methane concentration. The temperature of the column and the thermal conductivity detector (TCD) was fixed at 130 °C. The buffering cylinder pressure was changed according to the amount of remaining gas; therefore, a pressure regulator was used to regulate the gas pressure. Filters, valves and mass flow controllers were attached at the inlet and outlet of the metal hydride container. A thermocouple and a pressure sensor were used to measure the temperature of the metal hydride and the pressure of the gas phase in the container, respectively. A rotary vacuum pump and gas chromatograph were connected at the end of the gas line system.

To absorb and desorb the gas into or from the metal, the inlet and outlet flow rates were accurately controlled with mass flow controllers. However, if the absorption or desorption rate of the metal hydride was lower than the target flow rate that was set at the mass flow controllers, then the target value was not attained. In such a case, the mass flow controllers only limit the flow rate to the target flow rate. In most cases, the flow rate gradually converges at a constant that is kinetically specified, and it takes a long time to completely reach the constant. Therefore, experiments were performed until the difference between the absorption and desorption flow rates became 15 sccm.

Three different experiments were conducted in this study. The first experiment was to investigate the influence of methane on the metal hydride performance by varying the methane concentration. The second experiment was to measure the amounts of hydrogen stored with the methane concentration at 3%, which is equivalent to the output gas from a PSA system. The third experiment was to determine the methane concentration during hydrogen desorption from the metal hydride because a small amount of gas phase methane remains in the dead volume of the container.

In the first experiment, the relation between the methane concentration and the amount of absorbed hydrogen was measured. The detailed experimental conditions for the first experiment are listed as Ex. 1 in Table 1. 45.76 g of LmNi_{4.55}Mn_{0.12}Al_{0.15}Pd_{0.18} was used, which can absorb 7.28 L of pure hydrogen. Based on lanthanum-rich mischmetal (Lm) and nickel, the other
metals are contained to control the equilibrium pressure. The pressure-content-temperature (PCT) characteristics of the metal hydride at 30 °C are shown in Fig. 4. The PCT characteristics show the equilibrium pressure at various hydrogen contents (shown as the atomic ratio of hydrogen to metal). The plateau pressure is 0.21 MPaAbs for the metal hydride used in this study. After the metal hydride container was evacuated with the vacuum pump, hydrogen with 0-50% of methane was supplied from the buffering cylinder. The inlet gas pressure was regulated at 0.4 MPaG, which is equivalent to the PSA output pressure. The operation temperature was between 25-35 °C, which is near room temperature. Note that the temperature was controlled with a temperature controller, but the temperature fluctuated due to the exothermic process of the metal hydride. While the inlet flow rate was 300 sccm, the outlet flow rate was set to 150 sccm to prevent methane from remaining in the gas phase. The amount of absorbed hydrogen was calculated by integrating the hydrogen flow rate when hydrogen was released from the metal hydride.

The second experiment was performed to measure the amount of hydrogen absorbed during the proposed process. The metal hydride selectively absorbs hydrogen, so that other gases cannot be absorbed and remain in the gas phase. Contaminants then continue to accumulate during the absorption process if no off-gas is drained. In contrast, if the portion of the supplied gas in the metal hydride container is drained to the outlet as off-gas, then the contaminants are released and a higher hydrogen partial pressure is maintained to improve the absorption performance. Although increasing the amount of off gas easily flushes out the residual in the gas phase and results in higher hydrogen purity, the extra hydrogen that would have been absorbed into the metal hydride is also drained. Therefore, the amount of off gas should be minimized. In this study, the amount of hydrogen absorbed into the metal hydride was measured with and without off-gas. The experimental conditions are listed as Ex. 2 in Table 1. The gas supplied to the metal hydride consists of 97% hydrogen and 3% methane. The outlet flow rate was changed between 0.0 sccm and 9.0 sccm. The flow rate of 9.0 sccm corresponds to 3% of 300 sccm. The other experimental conditions were the same as the previous experiment. After absorption into the metal hydride was completed, hydrogen was released from the container to be measured.

The third experiment measured the methane concentration during hydrogen desorption from the metal hydride. In the container, the impurity gas is condensed because metal hydride absorbs only hydrogen, and the condensed impurity gas is present not only in the container but also in any dead volume, such as piping. To obtain pure hydrogen for supply to PEMFCs, it is necessary to purge such impurity gases in advance. Therefore, a small amount of hydrogen in the metal hydride should be released. In this study, the outlet gas from the metal hydride, into which

![Fig. 4 PCT characteristics of metal hydride (LaNi<sub>4.55</sub>Mn<sub>0.12</sub>Al<sub>0.15</sub>Pd<sub>0.18</sub>) at 30 °C](image)

<table>
<thead>
<tr>
<th>Table 1 Experimental conditions</th>
<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal hydride</td>
<td>LmNi&lt;sub&gt;4.55&lt;/sub&gt;Mn&lt;sub&gt;0.12&lt;/sub&gt;Al&lt;sub&gt;0.15&lt;/sub&gt;Pd&lt;sub&gt;0.18&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal hydride mass</td>
<td>45.76 g</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>Inlet gas pressure</td>
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<td>N/A</td>
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<tr>
<td>Temperature</td>
<td>25-35°C</td>
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<td>N/A</td>
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<tr>
<td>Inlet flow rate</td>
<td>300 sccm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outlet flow rate</td>
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<td>0.0, 4.5, 9.0 sccm</td>
<td>100 sccm</td>
</tr>
<tr>
<td>Contaminant</td>
<td>Methane, 0-50%</td>
<td>Methane, 3%</td>
<td>N/A</td>
</tr>
</tbody>
</table>

T=30°C  153.50(cc/g) (H/M=1.0)
hydrogen supplied with 3% methane was absorbed, was analyzed using gas chromatography. The experimental conditions are shown as Ex. 3 in Table 1.

3. Results and Discussion

Fig. 5 shows the absorbed hydrogen ratios at various methane concentrations. The absorbed hydrogen ratio is defined as the ratio of the amount of absorbed hydrogen at a specific methane concentration to the amount obtained when pure hydrogen is supplied. The absorbed hydrogen ratio decreased at higher methane concentrations. To investigate the reason for this, the theoretical absorbed hydrogen ratio was calculated from the PCT characteristics shown in Fig. 4, assuming that methane has no effect on the metal hydride, except for the decrease in partial pressure. The measured ratio of absorbed hydrogen deviates from the theoretical ratio at methane concentrations higher than 20%. It was thus concluded that methane gives some negative impact on the metal hydride. Therefore, the metal hydride can stably absorb hydrogen at methane concentrations less than 20% because large amounts of hydrogen remove methane from the metal hydride surface.

Fig. 6 shows the inlet flow rates and integrated volume of absorbed hydrogen (a) when pure hydrogen was supplied at 300 sccm and when hydrogen with 3% methane was supplied at a flow rate of 300 sccm and the outlet flow rates were (a) 0.0 sccm (b) 4.5 sccm and (c) 9.0 sccm. When the outlet flow rate was 0.0 sccm, the input flow rate suddenly dropped within 8 minutes and the integrated...
volume reached approximately 3 NL. In this configuration, when off gas was not drained, methane in the hydrogen accumulated as a gas phase in the dead volume of the metal hydride container and the gas line system. The total volume of methane in the supplied gas was estimated to be 0.09 NL, and the volume was calculated to be 18 cc at 0.4 MPaG. Thus, it is reasonable that methane was stored in the dead volume. However, the decrease of partial pressure lowered the amount of hydrogen stored compared with that when pure hydrogen was absorbed. When the outlet flow rates were 4.5 and 9.0 sccm, the higher inlet flow rate was maintained for longer time, compared with that when the output flow rate was 0.0 sccm. The integrated volume also reached a higher value because the residual methane was drained and the hydrogen partial pressure was maintained at a higher value.

The integrated values shown in Fig. 6 were calculated by integrating the difference between the supplied and drained gas flow rates. To precisely evaluate the absorbed hydrogen, the hydrogen absorbed into the metal hydride was released under various conditions and the amount of released hydrogen was measured, as shown in Fig. 7. The metal hydride used in this study released 7.28 NL of hydrogen when pure hydrogen was supplied, and the amount of released hydrogen was decreased to 2.98 NL when 3% of methane was included as a contaminant and the off gas was not drained. When the off gas was drained from the outlet of the metal hydride container, the amount of released hydrogen was increased as the flow rate of the off gas.

Fig. 8 shows the transient methane concentration during the gas release process when 3% of methane was supplied without off gas during the absorption process. It should be noted that almost 40% methane was detected at the very beginning of the release process, which implies the metal hydride selectively absorbs hydrogen. At the beginning of release, the methane concentration suddenly decreased. After release approximately 1.0 NL, the rate of concentration decrease became slower. If hydrogen with a methane concentration of less than 0.1% was required, for instance, then 0.9 NL of gas should be released at the beginning.

4. Conclusion

The influence of methane on the amount of hydrogen absorption into metal hydride was examined and the hydrogen purification performance during the hydrogen absorption and desorption processes was evaluated. Slight poisoning of the metal hydride by methane occurred at methane concentrations higher than 20%, while the metal hydride stably absorbed hydrogen with methane concentrations under 20%. The amount of absorbed hydrogen was significantly decreased when the hydrogen supply gas included 3% methane and the off gas was not drained. On the other hand, a small amount of off gas increases the amount of absorbed hydrogen. The gas released under no off gas condition contains a higher concentration of methane (40%) than the supplied gas at the beginning of the release process, and the concentration decreased as the release process proceeded to reach 0.1% at a total released amount of 0.4 L.

In future work, we plan to investigate the optimal absorption conditions, including the flow rate of off gas, and design a metal hydride container that can efficiently absorb hydrogen.

References