Computational Fluid Dynamics Simulation and Energy Consumption Analysis of Metal Hydride in Its Hydrogen Charging Process

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Metal hydride is an alloy that reversibly reacts with hydrogen gas. Because it has low hydrogen storage pressure, it can contribute to the abatement of compression power in the hydrogen charging process. Despite this fact, owing to the exothermic reaction in its charging process, a longer hydrogen charging time is required. As a countermeasure to this problem, a cooling process for the metal hydride bed is necessary to enhance the reaction rate of the hydrogen charging process. Considering this background, in this study, an energy consumption comparison between metal hydride and compressed hydrogen (conventional) is conducted. In addition, a mathematical model of the hydrogen charging process is developed to estimate the effect of the metal hydride cooling process on the hydrogen charging time. The mathematical model is validated by comparison with experimental results and used to simulate different cooling conditions (outside temperature: 233, 253, 273, and 298 K). It was found that metal hydride could reduce the compression power compared to compressed hydrogen (maximum reduction of 7.57 kWh/kg-H₂) and reduce the hydrogen charging time by removing reaction heat from the metal hydride tank (886 s at outside temperature 233 K, 1902 s at 273 K).

Key Words
Metal Hydride, Hydrogen Storage, Energy Consumption, CFD Simulation

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1. Introduction

Currently, the most common hydrogen storage method for fuel cell applications is compressed hydrogen. For example, commercialized fuel cell vehicles use 70 MPa of compressed hydrogen. Despite its short hydrogen charging time (3–5 min/4–10 kg-H₂), it has been reported that the compression power for hydrogen pressurizing accounts for 11–13% of the stored hydrogen energy content. This leads to energy loss and an indirect environmental impact.

Considering these problems of compressed hydrogen, metal hydride (MH) is a promising candidate that has the potential to replace compressed hydrogen storage. MH is an alloy that reversibly reacts with hydrogen gas and charges/discharges hydrogen into/from it. A notable feature of MH is its low hydrogen storage pressure. That is, the compression power can be reduced compared to compressed hydrogen because of the lower compression ratio. This leads to a higher energy efficiency and lower environmental impact of the hydrogen charging process.

In general, it is known that MH has a higher volumetric energy density than other energy storage devices. That is, the hydrogen storage in an MH tank can be stored in a small space. Thus, the utilization of MH to small mobilities that has limited place for energy storage device would gain the advantage in terms of the amount of stored energy compared to the other energy storage devices. Whereas it has been mentioned that for MH tanks, a disadvantage is that their weight energy density is less and fuel economy is worse, it was reported in a previous study that the weight gain of a Fuel Cell (FC) bicycle due to MH-tank use did not increase the power to assist. Therefore, the weight gain due to MH to small mobilities does not degrade their performance. Considering these estimations, because MH can enhance the energy efficiency of hydrogen storage and extend the operation time per charge of small FC mobilities, MH has the potential to be used for small FC mobilities.

However, focusing on the time required to charge hydrogen, MH has a longer hydrogen charging time compared to compressed hydrogen. The theory that the long hydrogen charging time is caused is as follows. In general, the hydrogen absorption reaction of an exothermic reaction into MH occurs if the hydrogen gas pressure, which is less than the inlet gas pressure, is higher than the equilibrium pressure. That is, the MH temperature during the absorption of the hydrogen increases, and the equilibrium pressure is greater. In addition, the difference between the hydrogen gas pressure and equilibrium pressure is one of the factors that dominate the reaction rate. Thus, as the equilibrium pressure increases due to the temperature rise of MH, the difference between the gas pressure and the equilibrium pressure decreases, resulting in a decrease in the reaction rate of hydrogen charging into MH and causing a long hydrogen charging time. Therefore, a greater difference between the inlet gas pressure and equilibrium pressure is more suitable for obtaining a higher reaction rate. Inversely, the hydrogen charging time at a smaller difference is increased.

In previous studies, reaction heat removal was proposed to prevent the equilibrium pressure increase due to the temperature increase of the MH, and to enhance the reaction rate of the hydrogen charging. For example, Chung et al. investigated the effectiveness of a heat pipe for reaction heat removal from an MH vessel by developing a 2D mathematical model. Fawzi A.M. Elhamshri et al. experimentally investigated and proved the effectiveness of heat removal from the MH tank on hydrogen charging time.

However, these and other studies did not point out the superiority of MH in terms of compression power compared to compressed hydrogen. Moreover, although previous studies investigated the reaction heat removal using an apparatus in the MH tank, to simplify and miniaturize the design of the MH tank, it would be better to not include the apparatus for the reaction heat removal in the actual MH tank. That is, heat removal by cooling the MH tank from the outside should be investigated.

Thus, in this study, the following objectives are set: (1) comparison of MH hydrogen storage and compressed hydrogen in terms of the hydrogen compression power consumption; (2) development of a mathematical model of the hydrogen charging process validated by experimental results; and (3) estimation of H₂ absorption time based on the cooling conditions from outside the MH tank using a mathematical model.

2. Methodology

2.1 Compression Power Calculation

The hydrogen compression power calculation methodology is explained in this section. Fig. 1 displays the compression power calculation scenarios in this study.

Case 1 is defined as onsite MH, which assumes that the hydrogen produced from the biomass plant (30 °C, 0.4 MPa) is charged into MH at 0.4 MPa. Case 2 is defined as offsite MH, which includes the hydrogen transportation process from a biomass hydrogen plant at 20 MPa. Case 3 is defined as offsite compressed hydrogen, which includes a hydrogen transportation process at 20 MPa and hydrogen storage into mobilities at 70 MPa as a conventional case.

For each scenario, the hydrogen compression power is
calculated in accordance with the following equations. First, it is known that the power required by the compressor can be calculated using the enthalpy difference before and after compression \(^7\). Thus, focusing on the enthalpy difference, the relationship between the enthalpy, specific heat, and temperature can be expressed as in Eq. (1).

\[
\Delta H = C_{pg} (T_2 - T_1), \quad (1)
\]

where \(C_{pg}\) is the specific heat of the hydrogen gas \([\text{J/kg K}]\), \(h\) is the enthalpy of the hydrogen gas \([\text{J/kg}]\), and \(T\) is the temperature \([\text{K}]\), subscript 1 indicates before compression and subscript 2 indicates after compression. In addition, the basic equation of adiabatic compression of an ideal gas can be expressed as in Eq. (2) assuming an ideal gas law.

\[
\frac{T_1}{P_1} = \frac{T_2}{P_2^\gamma}, \quad (2)
\]

where \(P\) is the pressure of the hydrogen gas and \(\gamma\) is the specific heat ratio. Using these two equations, the compression power of hydrogen gas, namely the enthalpy difference between the before and after compression, can be expressed as in Eq. (3) assuming an ideal gas law.

\[
W_{\text{comp}} = \eta \frac{C_{pg} T_1}{\eta} \left( \frac{P_2}{P_1} \right)^{1 - \gamma} - 1, \quad (3)
\]

where \(W_{\text{comp}}\) is the hydrogen compression power \([\text{J/kg}]\) and \(\eta (=0.7)\) is the efficiency of the compressor \(^8\).

### 2.2 Computational Fluid Dynamics (CFD) Simulation of Hydrogen Charging into MH

In this study, a mathematical model of the MH hydrogen charging process is developed with the following assumptions.

1. Hydrogen is assumed to be an ideal gas.
2. MH is considered a porous medium, which is assumed to be an isotropic medium with uniform porosity.
3. The thermophysical properties of \(\text{LmNi}_{13}\text{Mn}_{12}\text{Al}_{15}\) are similar to those of \(\text{LaNi}_5\), which is the same type (\(\text{AB}_5\)-type alloy) of MH as \(\text{LmNi}_{13}\text{Mn}_{12}\text{Al}_{15}\). This assumption to replace the thermophysical properties with other MHs has been used in a previous study \(^9\).
4. A local thermal equilibrium is assumed. That is, the temperature difference between the MH and hydrogen gas equals zero within the same location.
5. The parameter values listed in Table 1 are held constant.

In our experiment, MH stored in a cylindrical tank with a radius of 21 mm and height of 90 mm was used (see Fig. 2). Based on this configuration, the \(r\) radius to \(z\) height axisymmetric model was solved using a finite difference method using a 1 mm-square mesh size, which can be solved using the developed dynamic simulation software of CFD.

#### 2.2.1 Governing Equations

The time transition of the MH temperature is expressed by Eqs. (4) and (5).

\[
\begin{align*}
\varepsilon_\rho C_{rg} \frac{\partial T}{\partial t} + (1 - \varepsilon) \rho_s C_{ps} \frac{\partial T}{\partial t} & = \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\partial}{\partial r} \lambda_e \frac{\partial T}{\partial r} \right) \\
+ \frac{\partial}{\partial z} \left( \lambda_s \frac{\partial T}{\partial z} \right) - m (\Delta H + T(C_{pg} - C_{ps}))
\end{align*}
\]

\[
\lambda_s = (\varepsilon \lambda_e + (1 - \varepsilon) \lambda_s)
\]

where \(T\) is the temperature \([\text{K}]\), \(t\) is the time \([\text{s}]\), \(r\) is the radial direction, \(z\) is the axis direction, and \(m\) is the reaction rate.

### Table 1 Parameters used for simulation

| Parameter                          | Value     | Unit   |
|------------------------------------|-----------|--------|
| Specific heat of hydrogen gas \(C_{rg}\) | 1.428E+04 | J/kgK  |
| Reaction heat of MH \(\Delta H\)    | -1.539 E+07 | J/kg   |
| Specific heat of MH \(C_{ps}\)      | 4190      | J/kgK  |
| Porosity \(\varepsilon\)            | 0.500     | -      |
| Thermal conductivity of hydrogen \(\lambda_e\) | 0.3672  | W/MK   |
| Thermal conductivity of MH \(\lambda_s\) | 1.000   | W/MK   |
| Absorption rate coefficient \(C_a\) | 23.95     | s\(^{-1}\) |
| Activation Energy \(E_a\)           | 2.000E+04 | J/mol  |
| Empty MH density \(\rho_{emp}\)     | 4264      | kg/m\(^3\) |
| Saturated MH density \(\rho_{sat}\) | 4324      | kg/m\(^3\) |
| Permeability of the metal \(K\)     | 1.000E-08 | m\(^2\) |
| Molecular mass of hydrogen \(M_{H}\)| 2.016     | kg/kmol |
| Universal gas constant \(R\)       | 8.314     | J/molK |

![Fig. 2 Computational Domain](image-url)
rate of hydrogen absorption [kg/m$^3$/s].

The reaction rate of hydrogen absorption can be calculated using Eq. (6), which is widely used to estimate the reaction rate and has been validated with the experimental data by Mayer et al.\cite{10}.

\[ m = C_a \exp \left[ - \frac{E_a}{RT} \ln \left( \frac{P_g}{P_{eq_a}} \right) (\rho_{sat} - \rho) \right] \quad (6) \]

where $P_g$ is the hydrogen gas pressure [Pa], $P_{eq_a}$ is the equilibrium pressure of hydrogen absorption [Pa], and $\rho_s$ is the MH density [kg/m$^3$].

The equilibrium pressure can be defined using Eq. (7)\cite{11}.

\[ \ln \left( \frac{P_{eq_a}}{1000000} \right) = \frac{A}{T} - \frac{B}{T} \quad (7) \]

In terms of material balance, the following equations are applied as Eqs. (8) and (9).

\[ \frac{\partial (\rho_s V_{gr})}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho_s V_{gr} \right) + \frac{\partial (\rho_s V_{gz})}{\partial z} = -m \quad (8) \]

\[ (1 - \varepsilon) \frac{\partial (\rho_g)}{\partial t} = m \quad (9) \]

where $\rho_s$ is the hydrogen gas density [kg/m$^3$], $V_{gr}$ is the velocity of the hydrogen gas in the radial direction [m/s], and $V_{gz}$ is the velocity of the hydrogen gas in the axis direction [m/s].

The gas velocity and viscosity are calculated using Eqs. (10) and (11).

\[ V_{gr} = \frac{-K}{\mu_s} \frac{\partial P}{\partial r} \quad (10) \]

\[ V_{gz} = \frac{K}{\mu_s} \frac{\partial P}{\partial z} \quad (11) \]

\[ \mu_s = 9.05 \times 10^{-4} \times \left( \frac{T}{293} \right)^{0.68} \quad (12) \]

where $\mu_s$ is the viscosity of the hydrogen gas [Pa s].

2.2.2 Initial and Boundary Conditions

The following initial conditions were applied: $T_{ini} = 298.15$, $P_{ini} = P_{eq_a,ini}$, and $\rho_{s,ini} = \rho_{emp}$.

Note that the subscript ini indicates the initial condition.

For the boundary conditions of pressure, the nonslip boundary condition was applied as indicated in Eq. (13) except for the inlet (inlet pressure: 0.400 MPa), where $n$ refers to the normal direction.

\[ \frac{\partial P}{\partial n} = 0 \quad (13) \]

In addition, for the temperature boundary condition ($T_{wall}$), four types of temperature boundary conditions were applied to represent the different cooling conditions of the MH tank. That is, the CFD simulation was conducted four times under four different boundary conditions ($T_{wall} = 298.15, 273.15, 255.15, \text{and} 233.15$). Note that the equilibrium temperature equals to the temperature boundary condition.

2.3 Experimental Approach

To validate the hydrogen absorption mathematical model, a hydrogen charging into MH experiment was conducted. The MH tank is surrounded by the 298.15 K of water. The experimental results were compared with those of the mathematical model in terms of local temperature at $(r, z) = T_1(12, 76), T_2(12, 46), T_3(19.5, 46), \text{and} T_4(19.5, 16)$.

The MH alloy used in this experiment was LmNi$_{4.73}$Mn$_{0.12}$Al$_{0.15}$, an AB$_5$-type alloy, and an LaNi$_5$-type MH. One of the merits of LaNi$_5$-type alloys is their relatively low equilibrium pressure compared to other types of alloys. Thus, high-pressure hydrogen storage could be prevented.

Fig. 3 displays the experimental apparatus of the experiment.
3.2 Results of CFD Simulation

To validate the mathematical model of hydrogen charging into MH, the time transition of the local temperature at T1, T2, T3, and T4 was compared (mathematical model and experiment). Fig. 5 displays the time transition of the local temperature between the model and experiment.

Because the mathematical model predicted the same trends as the experiment, the mathematical model results were validated.

Based on Fig. 5, compared to T2 and T3, which have the same coordinates as the z point, the temperature decrease in the radial direction was approximately 20 K after 100 s of hydrogen absorption. Conversely, for T1 and T2 and T3 and T4, the temperature decreases in the z-axis direction were less than those of T2 and T3. That is, we found that the temperature decrease in the radial direction was greater than that in the axis direction. Therefore, effective heat removal in the radial direction is necessary. In future tasks, we will investigate an MH tank with a smaller radius to achieve a heat removal scheme.

Fig. 6 displays the temperature distribution of the MH tank after 100 s of hydrogen charging. As indicated in Fig. 6, the local temperature at the center of the tank was greater than that in the other areas. Thus, the reaction rate at the center of the tank was less than that in the other areas of the tank. That is, to promote a hydrogen charging reaction and reduce the hydrogen charging time, a suitable tank design that can remove the reaction heat from outside the tank or reaction heat removal at the center of the tank is necessary (Ex. an MH tank with a smaller radius).

Next, using this model, the hydrogen charging time into MH for each cooling condition (temperature boundary condition [K]: 298.15, 273.15, 253.15, and 233.15) was investigated, as displayed in Fig. 7. Note that the MH density increased with the MH charged hydrogen in it.

It was revealed that the cooling process of MH could...
reduce the hydrogen charging time, and the charging time was reduced at lower temperature boundary conditions. That is, the more heat removed from the outside of the tank, the shorter the hydrogen charging time. For example, based on the cooling condition, the 70% charging time (4302 kg/m³) was 886 s at 233 K, 1232 s at 253 K, and 1902 s at 273 K.

To investigate the effect of the heat removal from the MH on the hydrogen charging time, the reaction rate was investigated at several MH temperatures (see Fig. 8). It was found that a decrease in the reaction rate, causing a long hydrogen charging time, occurred as the temperature increased. Notably, a steep decrease in the reaction rate was observed in the high-temperature zone (greater than 298 K). Thus, hydrogen charging should be initiated at less than 298 K, where the steep decrease was not observed. Moreover, the reaction heat should be removed to avoid an MH temperature increase above 298 K and to maintain the reaction rate. Herein, a marginal decrease in the reaction rate was observed at 273–283 K, as indicated in Fig. 8. The fact that a reaction rate decrease was observed in the relatively low temperature range can be validated with the results of a previous study 12). Moreover, it is known that the temperature required to achieve the maximum reaction rate differs based on the hydrogen gas pressure as shown in Fig. 9 12). Thus, in future work, temperature control of the MH to achieve the required hydrogen charging time, based on the hydrogen gas pressure, should be considered.

4. Conclusions
In this study, an energy consumption calculation of hydrogen compression and CFD simulation of the MH tank were conducted.

The results indicated that in terms of energy consumption, the MH can reduce the compression power compared to compressed hydrogen by 7.57 (onsite MH versus compressed hydrogen) and 5.29 (offsite MH versus compressed hydrogen) [kWh/kg-H₂].

In addition to the energy consumption calculation, a mathematical model of hydrogen charging into MH was developed and validated by the experimental results of the time transition of the local temperature. Using the model, the simulated temperature distribution was investigated after 100 s of hydrogen charging. It was indicated that the reaction heat removal at the center of the tank could not be achieved by cooling the tank from the outside.

Moreover, the hydrogen charging time, based on the cooling condition, was estimated using a mathematical model. It was found that the cooler the boundary condition, the faster the charging time. That is, the greater the amount of reaction heat removed, the shorter the hydrogen charging time. However, the assumed cooling conditions such as 233 or 253 K, required a below freezing working fluid that could require additional energy input in its production stage.

Thus, in future work, a tank design that can remove the reaction heat from outside the tank or a tank design with reaction heat removal using a working fluid at greater than 273 K (e.g., water) from both the outside and center of the tank should be investigated to determine if it could achieve the same hydrogen charging time as tank cooling from the outside by a below freezing working fluid.

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