INTRODUCTION

The increasing requirements of various industries for hydrogen energy purity, hydrogen storage, and hydrogen purification have attracted much attention.1-3 With the development of household fuel cell systems and the widespread use of fuel cell vehicles, hydrogen and fuel cells' market size have increased year by year.4,5 High-pressure hydrogen tanks are the mainstream technology for storing hydrogen, but the danger and high cost of storing hydrogen at high pressure have been pointed out.6 Since hydrogen storage alloy (HSA) can store hydrogen up to about a thousand times its volume at room temperature and normal pressure, they have become the subject of numerous studies.7,8 Extracting hydrogen by reforming the gas obtained from biomass is an essential means of preparing hydrogen.9-11 Biomass, which includes agricultural and livestock waste, can produce fuel and is focused on as a clean distributed energy source.12,13 However, the gas obtained from biomass contains many impurities such as methane, carbon dioxide, and hydrogen sulfide, and it is reported that these impurities deteriorate the performance of fuel cells.14-16 There have been various studies to remove contaminants in hydrogen using the HSA. Dowaki et al use an adsorbent to establish a system to remove hydrogen sulfide impurities in the mixed gas.17 Saori et al take advantage of the HSA’s ability to absorb the only hydrogen and established a two-step purification system to...
separate impurities from hydrogen.\textsuperscript{18} It is also reported that the concentration of hydrogen sulfide in the mixed gas is necessary to reduce below 2 ppm. Otherwise, the voltage of the fuel cell will decrease by 2\% or more.\textsuperscript{19-21} Whether the lanthanum-rich mischmetal alloy can purify the hydrogen sulfide impurities in hydrogen to meet the corresponding criterion remains studied.

However, it is reported that when hydrogen derived from biomass is used, the absorption performance of the HSA deteriorates due to impurities.\textsuperscript{22} Besides interfering with the general process, contamination of the HSA usually affects the reaction and could prevent it from happening.\textsuperscript{23,24} Borozone et al perform a kinetic study on the HSA with carbon monoxide, which shows that carbon monoxide only has an influence on the absorption rate.\textsuperscript{25} Taniguchi and Ishida report that fluorination-treated hydrogen storage alloy suffers no poisoning, even for carbon monoxide concentrations as high as 100 ppm.\textsuperscript{26} F. Schweppe et al describe the absorption kinetics of various impurities on the HSA, and the results show that H$_2$S and CO have similar poisoning phenomena with the 1 ppm impurity concentration.\textsuperscript{27} Cristina et al show that 50 ppm H$_2$S has a nonnegligible effect on the HSA containing Lanthanum element.\textsuperscript{28} Research on the impact of H$_2$S on the HSA is still in the exploratory stage. Hydrogen purification processes expose the HSA to possible contaminants; it is crucial to understand how these impurities affect hydrogen sorption behavior. Since hydrogen sulfide concentration in the mixed gas depends on the feedstock, it is necessary to study the effect of different concentrations of hydrogen sulfide on the HSA. Besides, the cycling performance of the HSA has yet to be explored.

Accordingly, to evaluate the effect of low and high concentrations of hydrogen sulfide on the HSA comprehensively, the HSA is evaluated using pure hydrogen and hydrogen containing 1 and 100 ppm of hydrogen sulfide separately. A cycle experiment of repeating absorption and desorption is designed to evaluate the effect of multiple experiments on the HSA. The purification effect of the HSA on high-concentration mixed gas containing hydrogen sulfide is also evaluated. Furthermore, the performance degradation mechanism is analyzed using EDS and XPS.

## EXPERIMENTAL

### 2.1 Experimental materials and system

A lanthanum-rich mischmetal alloy was employed. It is one type of lanthanum alloy with higher durability against impurities and mixing rare earth metals can reduce refining costs than pure lanthanum. As shown in Table 1, based on lanthanum-rich mischmetal, the other metals were contained to control the equilibrium pressure. The pressure composition temperature (PCT) characteristics of the HSA in Figure 1 show the hydrogen contents at various pressure.

The schematic diagram of the experimental system is shown in Figure 2. The temperature, pressure, and flow rate in the system were controlled or measured by LabVIEW. The HSA was contained in a container designed to improve thermal conductivity. By inserting filters at both ends of the container, the HSA was prevented from leaking into the piping. The temperature controller controlled the temperature of the HSA. Valves and mass flow controllers were attached at the pure hydrogen gas cylinder, hydrogen sulfide gas cylinder, and outlet of the HSA container. A thermocouple and a pressure gauge were used to measure the HSA’s temperature and the gas phase pressure in the container. A vacuum pump was connected at the end of the gas line system.

### Table 1

| Hydrogen storage alloy | La | Ce | Pr | Nd | Ni | Mn | Al |
|------------------------|----|----|----|----|----|----|----|
| LaNi$_{1.73}$Mn$_{0.12}$Al$_{0.15}$ | 15.14 | 1.22 | 3.72 | 12.99 | 64.44 | 1.54 | 0.96 |

### Figure 1

PCT characteristics of the HSA at 30°C
During the pretreatment process, the activation treatment was performed. Due to the large particle initial size and small surface area of the HSA, the initial hydrogen absorption capacity is small. During the activation process, absorbs and releases hydrogen at 120°C for 5 cycles and then absorbs hydrogen at 0°C to make the HSA particles broken. When the amount of hydrogen absorbed reaches the maximum empirical value of 0.16 L/g, the activation is considered complete. The experiment started after confirming that the HSA is fully activated. For comparison, the experimental data of pure hydrogen supply and release before cycle experimental are recorded. The cycle experiment condition is shown in Table 2, divided into four steps: mixed gas supply, mixed gas release, pure hydrogen supply, and pure hydrogen release.

In the mixed gas supply experiment, a simulated gas mixture of pure hydrogen and hydrogen sulfide was applied instead of using the actual gas. Pure hydrogen was used as balance gas, and two types of mixed gas (1 ppm, 100 ppm) were prepared with the specified hydrogen sulfide concentrations. The hydrogen sulfide concentration of the supplied mixed gas was sampled before supplying to the HSA and measured with a gas chromatograph analyzer. The flow rate of the mixed gas was adjusted and measured by the mass flow controller simultaneously. The pressure was controlled as 0.4 MPaG by the regulator. Then, it passed through the filter and was supplied to the container. It was considered that if the hydrogen sulfide was not entirely absorbed after the mixed gas passed through the HSA, the accumulation phenomenon would cause the increasing concentration of hydrogen sulfide gradually. In order to avoid this phenomenon, the maximum flow of the outlet was set at 0.4 sccm. The concentration of hydrogen sulfide in the exhaust gas was measured to determine the HSA's ability to purify the mixed gas.

In the mixed gas release experiment, the gas in the HSA and the system was released entirely. The hydrogen sulfide concentration of off-gas was measured during release.

In the experiment of pure hydrogen supply and pure hydrogen release, pure hydrogen was absorbed and released to evaluate the HSA's absorption capacity. The cycling performance of the HSA was investigated by comparing the differences among the cycles.

### TABLE 2 Experimental conditions

| Stage in a cycle            | Step | Temperature (°C) | Pressure (MPaG) | Maximum flow of Inlet (sccm) | Maximum flow of outlet (sccm) | Maximum space velocity (1/h) |
|-----------------------------|------|------------------|----------------|------------------------------|-----------------------------|-------------------------------|
| Mixed gas supply            | 1    | 30               | 0.4            | 500                          | 0.4                         | 6088                          |
| Mixed gas release           | 2    | 30               | —              |                              | 500                         |                               |
| Pure hydrogen supply        | 3    | 30               | 0.4            | 500                          | —                           |                               |
| Pure hydrogen release       | 4    | 30               | —              |                              | 500                         |                               |

### 2.2 Performance evaluation and cycle experimental

The hydrogen sulfide concentration of the supplied mixed gas was sampled before supplying to the HSA and measured with a gas chromatograph analyzer. The flow rate of the mixed gas was adjusted and measured by the mass flow controller simultaneously. The pressure was controlled as 0.4 MPaG by the regulator. Then, it passed through the filter and was supplied to the container. It was considered that if the hydrogen sulfide was not entirely absorbed after the mixed gas passed through the HSA, the accumulation phenomenon would cause the increasing concentration of hydrogen sulfide gradually. In order to avoid this phenomenon, the maximum flow of the outlet was set at 0.4 sccm. The concentration of hydrogen sulfide in the exhaust gas was measured to determine the HSA’s ability to purify the mixed gas.
3 | RESULTS

3.1 | Rate of hydrogen storage and hydrogen release

In order to analyze the effect of different concentrations of hydrogen sulfide on the HSA, cycle experiments were carried out using H2 containing 1 and 100 ppm of hydrogen sulfide. After the mixed gas supply and mixed gas release experiment, the pure hydrogen storage and release rates were measured.

As shown in Figure 3, the inlet flow rates are first maintained at the maximum setting value, slowing down gradually. At the maximum flow rate, the temperature of the HSA is about 36°C, which is higher than the set temperature. As the flow rate decreases, the temperature decreased to 30°C gradually. It shows that the inlet flow rates of pure hydrogen and H2 containing 1 ppm of hydrogen sulfide decreased almost simultaneously, and the rate of decrease is almost the same. It is proved that 1 ppm of hydrogen sulfide does not affect the hydrogen storage rate. However, it was found that the inlet flow rates decay at an earlier time during 100 ppm cycle experiments. After the first cycle, a stationary state was reached where the complete absorption reaction occurs at a slow rate. No significant changes in the reaction were observed in further cycles.

The pure hydrogen release rates during cycle experiments are shown in Figure 4. The outlet flow rates have gone through a process from a rapid decrease to a slight decrease. The temperature is kept at the set temperature range, where the temperature is slightly lower than other conditions due to the faster release of pure hydrogen. It shows that the outlet flow rates of pure hydrogen and H2 containing 1 ppm of hydrogen sulfide decrease almost simultaneously, and the rates of decrease are almost the same. It is proved that 1 ppm of hydrogen sulfide does not affect the pure hydrogen release rate. The outlet flow rates of H2 containing 100 ppm of hydrogen sulfide decreased earlier and lower.

Figure 5 summarizes the results found for total absorption capacity in terms of the number of cycles performed. The storage capacity remains unchanged (6.65 L) while supplying pure hydrogen because the HSA has reached the maximum storage capacity during the activation treatment. The hydrogen storage capacity changes little during 1 ppm cycle experiments. It is proved that H2 containing 1 ppm of hydrogen sulfide had little effect on the absorption capacity of the HSA.

However, the outlet flow rates would not significant change from the second cycle.

3.2 | Evaluation of hydrogen storage capacity

Figure 5 summarizes the results found for total absorption capacity in terms of the number of cycles performed. The storage capacity remains unchanged (6.65 L) while supplying pure hydrogen because the HSA has reached the maximum storage capacity during the activation treatment. The hydrogen storage capacity changes little during 1 ppm cycle experiments. It is proved that H2 containing 1 ppm of hydrogen sulfide had little effect on the absorption capacity of the HSA.

The hydrogen storage capacity was reduced by about 20% in the first cycle of 100 ppm cycle experiments. With the increase of experimental cycles, the hydrogen storage capacity did not continue to decrease dramatically. It is proved that H2 containing 100 ppm of hydrogen sulfide would reduce the absorption capacity and reach a stationary state.
3.3 | Purification of hydrogen

In order to detect the content of hydrogen sulfide, the off-gas was collected in the aluminum gas bag (GL Sciences). The hydrogen sulfide concentration was measured with a gas chromatograph analyzer (GC-2014, Shimadzu Corp.). In order to desorb the hydrogen sulfide adsorbed inside the gas bag, the measurement was performed after warming for 30 minutes with an electric blanket before analysis.

In order to analyze the purifying capacity of the HSA, the off-gas at the steps of mixed gas supply, mixed gas release, and pure hydrogen release were sampled in a gas pack to measure the hydrogen sulfide concentration. As a comparative experiment, silicon dioxide was put into the container to experiment with the same condition. Table 3 shows the results of the 6th cycle experiment. It shows that the concentration of hydrogen sulfide remains almost unchanged with silicon dioxide. However, the hydrogen sulfide is not detected at any step using the HSA. It shows that silicon dioxide does not adsorb hydrogen sulfide and the HSA can adsorb hydrogen sulfide. It also shows the validity of the experimental design. Additionally, since the gas chromatography analyzer used in this study could detect hydrogen sulfide above 0.2 ppm, it is proved that the concentration of hydrogen sulfide in the off-gas and the gas at the time of release is less than 0.2 ppm. From this, it is determined that hydrogen could be highly purified with the HSA repeatedly.

| Material                  | Stage in a cycle | Step | 1 ppm of H₂S | 100 ppm of H₂S |
|---------------------------|------------------|------|--------------|----------------|
| Hydrogen storage alloy    | Mixed gas supply |      | 0 ppm        | 0 ppm          |
|                           | Mixed gas release| 2    | 0 ppm        | 0 ppm          |
|                           | Pure hydrogen release | 4 | 0 ppm  | 0 ppm  |
| Silicon dioxide           | —                | —    | —            | 115.5 ppm      |

4 | DISCUSSION

4.1 | Analysis of the sulfur element distribution

The surface and cross-section of the HSA were observed by SEM, then the distribution of the sulfur element was analyzed using EDS. The accelerating voltage was 15 kV, and the beam current was adjusted to 2 nA to obtain the maximum signal. The EDS maps were acquired at a resolution of 1024 × 768 pixels. In this condition, the acquisition time of a graph is over two hours. As the results shown in Figure 6, the green dots show the distribution of the sulfur element.

As the result shown in Figure 6A, the activated alloy presents a relatively uniform powder state. It could observe that the sulfur element was evenly distributed on the HSA surface from Figure 6B. It is confirmed that the sulfur element was adsorbed on the surface of the material. The decreased reaction rate is considered that the adsorption of hydrogen sulfide on the HSA, resulting in a reduced surface area for the reaction. As shown in Figure 6C and D, it could be observed...
that the sulfur element was distributed in the HSA section. It is proved that the sulfur element is not only distributed on the surface but distributed inside the HSA. This fact shows that the purification mechanism of hydrogen sulfide is that the HSA absorbs the sulfur element.

**4.2 Analysis of chemical composition**

XPS was carried out on the HSA to determine the chemical compositions of the sulfur elements. 4 kV voltage was used to accelerate Ar+ ions and sputter-etch the samples. Different energies gave different etching speeds; sputter time was adjusted to 1 second to obtain information from the different depths.

Figure 7A shows that the S2p characteristic peak is caused. Figure 7B shows the spectrums of different sputtering depths. According to the spectrums, it is determined that the chemical composition is NiSO₄ and NiS, respectively. Since surface and shallow sputter spectra have NiSO₄ peak and deep sputter spectra only have NiS peak, the chemical composition inside the HSA is NiS. The peak of NiSO₄ is caused by oxidation due to exposure of the sample to oxygen in the air. Since the first and second sputter spectra have two peaks and the peak of NiSO₄ gradually decreases, it can be inferred that the chemical composition of the surface before oxidation should be NiS. According to the peak intensity, the sulfur element is distributed in the HSA evenly.

The adsorbed H₂S on the surface would prevent the dissociation of hydrogen molecules to atoms on the surface. If H₂S concentrates only on the surface, it will further deteriorate the performance of the HSA. The uniform distribution of the sulfur element into bulk causes the HSA's performance to remain at a certain level after deterioration.

**5 CONCLUSIONS**

Absorption-desorption cycle experiments were conducted using a mixed gas with hydrogen sulfide concentrations of 1 and 100 ppm, and the effects on the HSA were investigated. The following conclusions can be drawn:

When the impurity concentration of hydrogen sulfide is 1 and 100 ppm, the HSA can remove hydrogen sulfide altogether to obtain purified hydrogen.

1 ppm hydrogen sulfide has little effect on the HSA, the hydrogen storage capacity, absorption rate, and release rate have almost no change after absorption-desorption cycle experiments.

With hydrogen sulfide concentrations of 100 ppm, the hydrogen storage capacity, absorption rate, and release rate were all reduced, but since the second cycle, it was no longer continuing to decrease.

The purification effect is due to the absorption of H₂S by the HSA. The deterioration of the HSA is attributed to the formation of NiS on the surface. The HSA's performance retention to a certain extent after deterioration is attributed to the uniform distribution of the sulfur element.

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