Preliminary study on hydrogen storage for fuel of fuel cell using Fe$_3$Al metal hydride system

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Abstract. Fe$_3$Al alloy for hydrogen storage was successfully synthesized from Fe (70 wt%) and Al (30 wt%) through ball-mill method in 5 hours milling and Ball to Powder Ratio (BPR) 10:1 to produced mechanical alloy. The results was confirmed by XRD diffraction pattern at $2\theta = 44.791^\circ$ (10) which is characteristic peak of Fe$_3$Al. The material was applied on hydrogen storage to form metal hydride in which at various temperature and pressure. The Fe$_3$Al alloy performance for hydrogen storage for fuel cell application was indicated from the capacity of hydrogen adsorption and the ability to supply hydrogen for fuel cell. Characterization by using SEM-EDX on adsorption used alloy showed that Fe$_3$Al Alloy has homogeneous surface and no cracks revealed. XRD pattern of alloy after being used to adsorb hydrogen showed a typical pattern at $2\theta = 44.667^\circ$ (11). Based on the results it can be concluded that hydrogen storage capacity increases with increasing temperature and pressure, and the average adsorption capacity were 58%. Hydrogen storage by the metal hydride method has met the storage criteria established by the US Department of Energy (DOE) as clean and efficient urban energy for the future.

Keywords: metal hydride, mechanical alloying, fe$_3$al, adsorption.

1. Introduction

Energy is a basic need of the world today for all residential, commercial, industrial and transportation activities [1] but the energy used today, most use fossil fuels that cannot be renewed. High population growth impacts on increased energy consumption. This causes fossil fuels to thin out and cannot meet human needs in the future [2], [3] so that sustainable alternative energy is needed to replace the role of fossil fuels [2]. On the other hand fossil fuels also have a negative impact on the environment caused by exhaust emissions in vehicles in the form of CO [4].

Hydrogen as an element whose abundance is very high in nature and simplest in the periodic table, with density (in the form of gas) of 0.0899 kg/Nm$^3$, which is 15 times lighter than air. Hydrogen is a fuel with a wide range of flammability, both in the air, from 4-75%, and in oxygen, from 4-95%. Hydrogen is also a high energy density (per mass unit) with Higher Heating Value (HHV) of 3.54
kWh/Nm3 (39.42 kWh/kg), which is 2.5 times higher than methane and 3 times higher than gasoline [5]. These properties make hydrogen have the potential as a very promising alternative fuel source for the future and become one of the right solutions in overcoming fuel availability problems [6].

However, one of the limitations of exploiting hydrogen is the need for economically safe, safe and comfortable storage media because hydrogen is highly reactive to direct air contact [7]. The US Department of Energy (DOE) in 2017 sets out five main factors (such as gravimetric and volumetric capacity, operating temperature, system life cycle and filling time) that need to be considered as efficient hydrogen storage [8]. The three main hydrogen storage methods such as compressed hydrogen gas (CGH₃ and CeH₃), liquid hydrogen and solid storage (MH₂, such as metal hydrides) which have attracted many researchers since they can be operated at low temperature and pressure [9]. The MH₂ system is considered promising with the hydrogen molecule chemisorption tightly bound into the material lattice and by physical adsorption on the material surface [8] metal hydride has a high hydrogen (H₂) storage density compared to hydrogen or liquid hydrogen [9], [10]. The other methods of hydrogen storage are in formic acid and methanol [11], carbon nanostructure [12] and lithium decorated zeolite [13].

Fe and Al metals are very abundant metals on earth and the price is affordable. Fe and Al metals are atoms which have valence electrons 3+. This condition is very interesting to study the ability to bind hydrogen atoms to form metal hydrides. Based on these characteristics, a study of the hydrogen gas storage and release process was carried out using the metal hydride method using Fe-Al metal alloys.

2. Methods
Fe-Al alloy is synthesized using mechanical alloying method as much as 2.5 grams of mixture of Fe (iron) (99.99% purity) and Aluminum (99.99% purity) with a percentage ratio of Fe:Al weight is 70:30. The tool used in Mechanical Alloying is high energy milling type 3D elliptical milling machine (HEM- E3D). The mechanical alloying process is carried out with BPR (Ball to Powder Ratio), which is 10:1 and using the PCA (Process Control Agent) of methanol. The mechanical alloying process is carried out by milling for 5 hours [14]. After Fe₃Al alloy was obtained, characterization was then performed to analyze the structure, and morphology of the particle using X-Ray Diffraction (XRD) and SEM-EDX. Storing hydrogen were performed by weighing the empty tube that has been vacuumed, and then the tube is filled with Fe₃Al alloy and then vacuumed again and weighed. Hydrogen gas is flowed into a vial containing Fe₃Al alloy at a temperature of 30°C, 40°C, 50°C. After the hydrogen flow process, the gas is released. The procedure is also done for pressure variations 2 and 3 bars.

3. Result and discussion
3.1 Manufacture of Fe-Al alloy and results of the analysis using XRD
The manufacture of Fe-Al Alloy using mechanical alloying method with HEM-E3D type ball milling tool that utilizes collisions between balls. The mechanical alloying process is influenced by several parameters such as BPR ratio, ball size milling time. BPR is a ratio of the weight of the ball and the weight of the material adjusted to the volume jar at least <50% or <60%. In the manufacture of Fe-Al alloys a ratio of 10:1 is used. The size of the ball used also gives a significant effect because the smaller the size of the ball, the greater the surface area that is 5mm in diameter for Fe (10-40 mesh) and aluminum metal (<1 mm) is used. While the milling time is self-based on the structure of the material to be used such as Fe and Al metal alloys takes <30 hours [15].

The making of metal alloys was carried out with a mixture of Fe 70 wt% and Al metal 30 wt% at room temperature and 5 hour milling time. In the process of mechanical milling, 2 mL of methanol is added as a process controlling agent (PCA) in the liquid phase which is adsorbed on the metal surface which causes a reduction in energy to control the milling process to run properly [16]. The results of milling Fe-Al metal alloys were obtained in the form of fine black powder as seen in Figure 1.
The next process after milling is heating sample using oven vacuum at 0.4 bar and 70°C for 2 hours to evaporate methanol. Mass of alloy after heating was 35.3788 g. The results of metal alloys were characterized by XRD analysis as seen in Figure 2.

X-ray diffraction patterns for Fe-Al alloys in Figure 2 have a similar pattern with the report before [17]. This value is also in accordance with the value JCPDS No. 06-0695 (Fe₃Al) [18], [19] and similar values were also shown in the study of Wei et al (2017) [20], the diffraction peaks that are characteristic of Fe₃Al alloys are at diffraction angles around 37 (42-3), 45 (110), 66 (200), 83 (211). However, in the synthesized alloy at this time, the diffractogram peak only appears at diffraction angles around 37, 45 and 66 for a 5 hour milling time having a sharp peak with high intensity with a crystal size of 31.549 nm.

3.2 The SEM-EDX analysis on Fe₃Al alloy after hydrogen adsorption

According to the Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) test results for Fe₃Al metal alloys after adsorption of hydrogen, can be seen that iron and aluminum have been evenly mixed. In Figure 3, there are other atoms such as carbon atoms and oxygen where they come from the remaining methanol used as PCA in the milling process.
Figure 3. SEM and EDX analysis results on Fe₃Al alloy after the process of adsorption of hydrogen

The percentage of iron and aluminum atoms looks lower than carbon and oxygen atoms. This shows that most of the Fe and Al have changed to form Alloy. The percentage of Fe and Al mass detected from EDX did not match the actual percentage of Fe and Al (70:30). This is because the data on EDX only measures the spot from the surface. The higher percentage of carbon and oxygen indicates the presence of non-volatile methanol which partially covers the surface of the Fe₃Al alloy. Figure 3 shows a magnification of 20.20 Kx having a pore as large as it can be concluded that Fe₃Al alloy has a pore size of < 0.2 μm. The Fe₃Al alloy has a rough and thick surface that is not uniform. In Figure 3 there were also no cracks or cracks on the surface area of the Fe₃Al alloy. This indicates a strong bond between Fe-Al metals.

3.3 Qualitative analysis of adsorption of hydrogen from Fe-Al alloy and XRD characterization results for metal hydride

Initially hydrogen gas is flowed into the reactor tube containing Fe-Al alloy for 60 seconds with variations in temperatures of 30°C, 40°C, 50°C and variations in pressure 1, 2, 3 bars. Hydriding a metal is carried out by direct dissociative chemisorption and physisorption. Solid state storage of hydrogen fuel occurs absorption in the gap metals and metal alloys or adsorption at surface areas metal [10] so then hydrogen adsorption capacity was measured. In process of hydrogen adsorption in the Fe-Al alloy, hydriding process it turns into metal hydride (FeH, FeH₂, FeH₃ or AlH₃) [21]. A typical reversible interaction between metal/alloy and hydrogen can be written:

\[
M + \frac{x}{2}H_2 \rightarrow MH_x + Q
\]

Where M is a metal, an intermetallic alloy, or a solid solution, x is a positive whole number, MHx is the formed hydride and Q is the heat of reaction [22]. The condition and shape of metal hydride before and after hydrogen absorption is characterized using XRD as shown in Figure 4. In Figure 4 it can be seen that the typical peak after hydrogen gas adsorption process is almost the same as the diffraction pattern before the adsorption of hydrogen gas.

Before the adsorption process obtained a typical peak in the diffraction pattern 44.791 (10) and after the process of adsorption of hydrogen gas obtained a typical peak on the diffraction pattern 44.667 (11) with a crystal size of 31.209 nm. This is because the bond between metals and hydrogen is not a chemical bond which is only bound as a physical bond so that the bond is easily released and the shift in the diffraction pattern is unreadable.
Figure 4. X-ray diffraction pattern in Fe$_3$Al alloy (a) before (b) after the process of adsorption of hydrogen gas

3.4 Determination of hydrogen storage capacity from Fe-Al/H$_2$ metal hydride

Determination of hydrogen adsorption capacity in the Fe-Al alloy system is carried out at various temperatures and pressures. Based on Table 1, it can be seen that in general, hydrogen adsorption capacity increases with increasing temperature and pressure. However, the adsorption of hydrogen in the initial conditions with a temperature of 30°C and pressure of 1 bar has a greater capacity. This is because the alloy material is still new so that hydrogen is absorbed maximally. With repeated absorption and release of hydrogen, hydrogen absorption capacity decreases because there is hydrogen retained in alloy materials. At the higher the temperature and pressure the storage capacity increases, because at the higher temperature and pressure can open the pores so that more hydrogen gas can be stored and released again.
Table 1. Results of measurement of hydrogen gas storage capacity on effects of temperature and pressure.

| No | Pressure (Bar) | Temperature (°C) | Adsorption capacity |
|----|----------------|------------------|---------------------|
| 1. | 1              | 30               | 60%                 |
| 2. | 1              | 40               | 75%                 |
| 3. | 1              | 50               | 56%                 |
| 4. | 2              | 30               | 52%                 |
| 5. | 2              | 40               | 55%                 |
| 6. | 2              | 50               | 60%                 |
| 7. | 3              | 30               | 38%                 |
| 8. | 3              | 40               | 52%                 |
| 9. | 3              | 50               | 78%                 |

The relationship between temperature and pressure on hydrogen adsorption capacity of Fe-Al alloy is shown in Figure 5 and 6. From Figure 5 and 6 can generally be seen that the average storage capacity increases with increasing temperature and pressure with the average storage is 58 wt%.

Figure 5. Graph of influence of temperature on adsorption capacity of hydrogen
4. Conclusions
a. The Fe$_3$Al alloy was successfully synthesized with an alloy of Fe 70% b/b and Al 30% b/b with a milling time of 5 hours and Ball to Powder Ratio (BPR) 10:1 and a flame time of 3 minutes and 1 minute rest time. Based on the results of XRD characterization it is known that the typical diffraction pattern at 44.79° shows a typical peak for Fe$_3$Al.

b. Performance of Fe$_3$Al alloy as hydrogen storage and release can be seen from the hydrogen storage capacity. In general, hydrogen storage capacity increases with increasing temperature and pressure. Based on the results of the study, the average Fe$_3$Al alloy has a hydrogen adsorption capacity of 58 wt%.

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