



## Hydrogen Absorbing Material in Carbonaceous-Metal Hydride

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**Abstract.** One of the most promising materials for storing hydrogen in solid state would be included in metal-carbon composites. In order to obtain nanocrystalline metal particles encapsulated by crystalline or amorphous carbon, mechanochemical synthesis of zirconium-carbonaceous composites and alkali metal-carbonaceous composites was performed. For zirconium-carbonaceous composites, only zirconium-carbon black composite absorbed more hydrogen than expected for a mere mixture with the same composition. The higher hydrogen capacity on the zirconium-carbon black composite would be due to some specific sites on the carbonaceous material created during the milling. Another effect of the composite formation was stabilization of zirconium, that is, the composites did not ignite in air. On alkali metal-carbonaceous composites, carbon black has superior effect in composite formation compared with graphite in which some cooperative effect was only detected on alkali metal-carbon black composite. The effect of the carbonaceous composite formation was resistance to air and anti-sticking characteristics to balls and the wall of the vial during the ball milling. Copyright © 2006 Teknik Kimia UNSYIAH

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### INTRODUCTION

Hydrogen has many potential energy uses, including powering non-polluting fueling aircraft, heating homes and offices, and vehicles. For hydrogen fuel storage and particularly in transportation systems, a simple, direct, and reversible reaction is desired. However, the main difficulty to use hydrogen as a transportation fuel is the lack of suitable means of storage. Storage in solid matter offers the advantage of safer and easier handling of hydrogen. This challenge has given a new direction to hydrogen researchers. The application of mechanochemical methods is known to be helpful in the preparation nano-sized materials for various classes of chemical compounds. When metallic particles are subjected to high-energy ball milling, the particles are fractured into smaller fragments that are then cold-welded together. By repeated fracture and welding, a new

surface or interface is generated. Some of the benefits of using ball-milling technique are: (i) the ease of formation of several alloys (Liang et al., 1998, Abdellaoui, 1998) and hydride phase (Tessier et al., 1998); (ii) the production material in the nanocrystalline and/or amorphous state, with various amounts of dislocations and special defects with high binding energy for hydrogen (Orimo et al., 1997, Zaluski et al., 1995); (iii) the generation of fresh and highly reactive surfaces during the milling operation, which increase the hydrogen absorption rate (Aoyogi et al., 1995); and (iv) the ease of formation of nanocomposite in which a compound is intimately mixed with another element or compound that can act as catalyst to improve the hydrogen absorption kinetic (Zaluski et al., 1995, Gross et al., 1997).

At present, the interest in metal-carbon systems has substantially increased. This is being a great extent due to the possibility to

obtain nanocrystalline metal particles encapsulated or intercalated by crystalline or amorphous carbon. Among the variety of such compositions, much interest is devoted to systems in which zirconium and alkali metal are used as nanocrystal metal particle. Investigation and preparation of encapsulated/ intercalated hydrogen material substances is connected with a series of unique properties characteristic of this sort of material defining the possibility of their commercial application.

Application of mechanical milling to zirconium-carbonaceous composite and alkali metal- carbonaceous composite under hydrogen atmosphere can be expected to create vast amounts of defects and strain in the lattice, and so a large number of dangling bonds of carbon will be occurred. Therefore, there is a possibility that mechanical milling under hydrogen gas atmosphere assists the carbon to absorb a large amount of hydrogen. However, the milling method that performed on carbonaceous materials will also collapse any structure of them so that their ability to adsorb hydrogen would also decrease at certain milling time.

## EXPERIMENTAL

### *Samples preparation*

The preparation of zirconium-carbonaceous composite was carried out by mechanical milling of samples in a Fritsch 6 planetary ballmill. In this Fritsch 6 planetary ballmill, both stainless steel balls and vial were used. The vial was equipped with a connection valve for evacuation of gas inside it and introduction of hydrogen gas as well. The milling was carried out at room temperature. First, zirconium hydride was prepared from zirconium (lump) under high pressure of H<sub>2</sub> gas (about 3.5 MPa) at 623 K for 12 h. All the material handling (including weighing and loading) was

conducted in a glove box/globe bag containing nitrogen.

Next, the preparation of zirconium-carbonaceous composite was started from zirconium hydride together with commercially available graphite and carbon black by mechanical milling. Before used, each graphite and carbon black had been evacuated at 383 K for about 2 h in order to remove water vapor or other impurities contained in it. The milling process was carried out at speed of 300 rpm for periods of 30 min, and because this is a very energetic process, the machine was stopped every 10 min in order to cool down the vial and the sample to room temperature. When the milling was completely finished, the mill vial was opened to take out the sample in a nitrogen glove box. For further characterization and measurement the sample was put in a sealed-bottle and stored in globe box.

The mechanical milling technique was also applied to direct synthesis of Li<sub>1.6</sub>Al<sub>0.8</sub>Ni<sub>0.2</sub>H<sub>4</sub> from element of lithium, aluminum and nickel under hydrogen atmosphere. Afterwards, Li<sub>1.6</sub>Al<sub>0.8</sub>Ni<sub>0.2</sub>H<sub>4</sub>-carbonaceous composites was prepared under 0.5 MPa hydrogen pressure in milling apparatus for another 30 min. Carbonaceous materials that were used for composite formation were commercially available graphite (Kishida Chemical, Osaka, Japan) that had an average particle size of 75 μm with nominal purity of 99% and carbon black ("furnace black" of sigma) which had an average particle size of 325 mesh. For each batch about 7.5 g of the elements was loaded into the vial. The ball-to-powder ratio was maintained at 30:1 during the process. Before introducing hydrogen gas, the vial of the ball mill was evacuated by a rotary pump and then filled with hydrogen gas (99.99%) to a pressure of 0.5 MPa. The milling process was carried out at a rotation speed of 400 rpm and interrupted every 10 minutes to cool the vial for 15 min.

### Samples Characterization

Differential thermal analysis (DTA) and thermogravimetry analysis (TGA) were performed simultaneously on Rigaku Thermo Plus TG 8120 under 10% hydrogen/argon gas with  $10 \text{ K min}^{-1}$ . Alumina pans were used with the sample held in the apparatus and repetition of TG measurement was performed in order to confirm the reversibility of hydriding/dehydriding process. The first heating process was performed right after the sample inside the heater column was evacuated and flushed by flowing 10% hydrogen/argon gas for several times. The other heating process was carried out after the sample was cooled to reach room temperature under 10% hydrogen/argon gas.

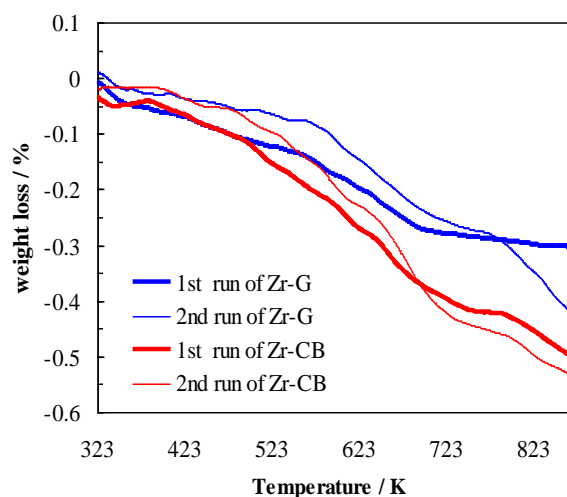
Hydrogen sorption pressure-composition isotherms were collected by a Sieverts type apparatus equipped with two pressure gauges the full ranges of which were 10 and 1000 Torr (760 Torr=101.3 kPa). Principle of the measurement follows the historical Sieverts' method. The adsorption isotherms were measured at 298 K and equilibrium pressures ranged from 0 to 100 kPa.

## RESULTS

For zr-carbonaceous composite system, the preliminary analysis of zr-carbonaceous composite that measured by TG-DTA was shown in Figure 1 zr-carbon black composite absorbed more hydrogen compared with zr-graphite composite. The reversibility on both first cycle and second cycle was similar. Therefore, addition of carbon black and graphite as the carbonaceous source in the composite retained the reversibility of weight loss. The result of TG-DTA as preliminary analysis was confirmed by hydrogen adsorption isotherm in Figure 2.

It has been mentioned formerly in experimental procedure, that both

zirconium-graphite composite and zirconium-carbon black composite was produced through mechanical milling of zirconium with graphite or carbon black. Thus, in order to clarify whether the expected isotherm by combining zirconium and graphite/carbon black was similar to observed ones or not, the figure regarding to linear combination was constructed as can be viewed in Figure 2. It was observed in this figure that the expected isotherm of zr-graphite composite determined by linear combination was higher than that of the observed isotherm.

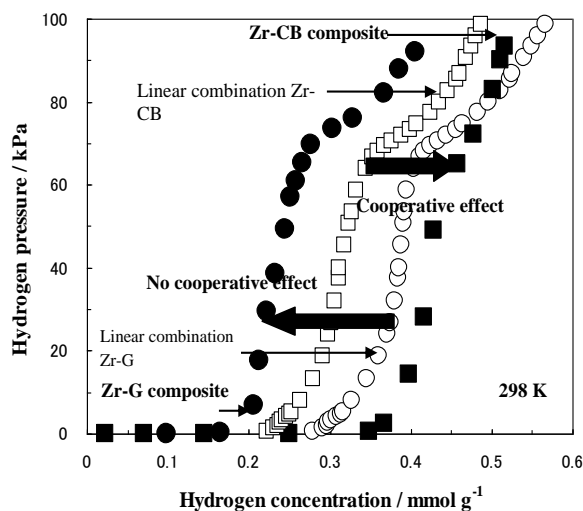


**Figure 1.** TG-DTA measurements of zr-graphite/carbon black composites

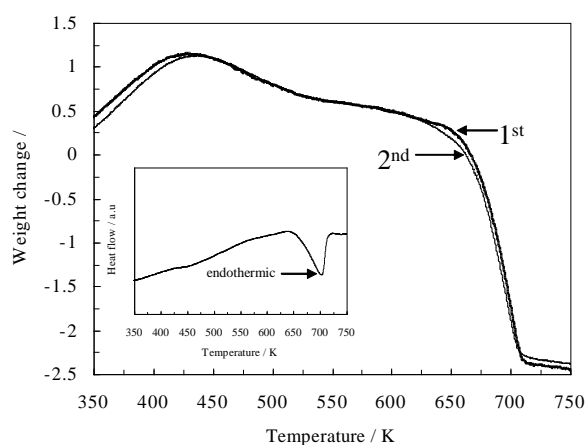
On the other hand, the observed isotherm of zr-carbon black at low hydrogen pressure in Figure 2 was promoted and became higher than that of the expected isotherm. According to data from the linear combination, it can be concluded that on zr-carbon black composite some cooperative effects were detected, but it was not detected on zr-graphite composite. The cooperative effects on zr-carbon black composite were speculated due to higher dispersion carbon black. While, small deterioration in hydrogen capacity of zr-graphite composite would be due to the collapse of graphite phase.

The maximum H/Zr ratio reached on zr-graphite composite and zr-carbon black

composite at hydrogen pressure of 93 kPa was around 0.26, and 0.31, respectively. This ratio was lower than the stoichiometric value.



**Figure 2.** Hydrogen absorption isotherm of zirconium-graphite/carbon black composites

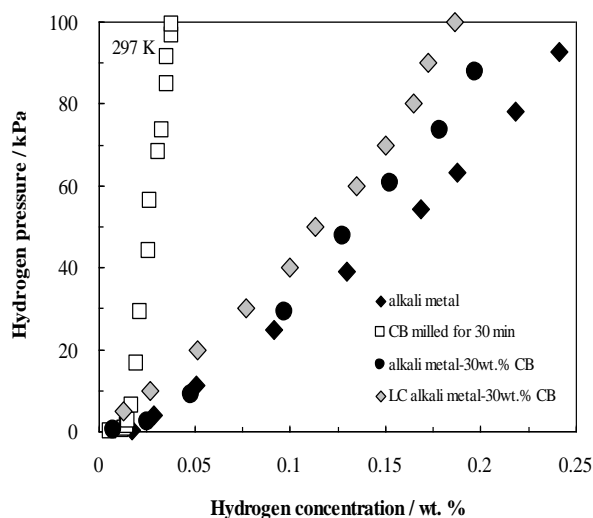


**Figure 3.** TG-DTA measurements of alkali metal-30wt% graphite composite

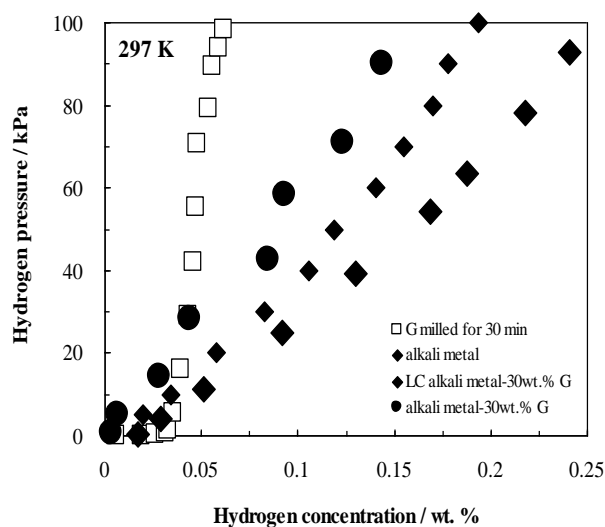
The system for alkali metal-carbonaceous composite is discussed to compare with zirconium-carbonaceous composite. Figure 3 shows that the weight change of alkali metal-30wt% graphite had a good reversibility and reached the weight change of 2.42 wt.% with one endothermic peaks around 720 K. The decomposition temperature was slightly shifted to higher temperature in the case of alkali metal-carbon black composite. However, such

shift was not observed for alkali metal-graphite composite.

In Figure 4, expected isotherms by linear combination (LC) of the isotherms for alkali metal and carbon black were compared with observed ones. The observed hydrogen capacity of alkali metal-30wt.% CB was a little bit higher than the expected hydrogen capacity calculated from linear combination (LC alkali metal-30wt.% CB) under low hydrogen pressures.



**Figure 4.** Hydrogen absorption isotherm of alkali metal hydride and alkali metal-30wt%-carbon black composites



**Figure 5.** Hydrogen absorption isotherm of alkali metal hydride and alkali metal-30wt%-graphite composites

**Table 1.** Comparison of alkali metal hydride ( $\text{Li}_{1.6}\text{Al}_{0.8}\text{Ni}_{0.2}\text{H}_4$ ) milled for 8 h with graphite (G)/carbon black (CB) and without.

Samples	Weight change (%)	Reversibility	Contacting with air	Preparation
Alkali metal	4.00	yes after run 1	tend to burn	easily to stick on balls/wall of vial
Alkali metal-30wt.% CB	2.9	Yes	not burning	not sticking
Alkali metal-30wt.% G	2.4	Yes	not burning	not sticking

On the contrary of alkali metal-carbon black system, the hydrogen capacity measured by sorption isotherms for alkali metal-30wt.% graphite was lower than the expected hydrogen capacity calculated from linear combination as shown in Figure 5. The result that the weight loss of alkali metal-30wt.% carbon black was higher than that of alkali metal-30wt.% graphite is similar to zr-carbonaceous composites system that the addition of carbon black had a preferable effect in retaining hydrogen capacity compared with the addition of graphite.

Finally, the effect of carbonaceous material addition on alkali metal hydride was confirmed as summarized in Table 1. As summarized in Table 1, the weight loss value for alkali metal-30wt.% carbon black and alkali metal-30wt.% graphite were close to 2.8 wt.%, which value was expected for the composites with the contribution of graphite or carbon black to hydrogen sorption neglected. Besides, the addition of graphite during preparation process had some advantages. The use of 30 wt.% graphite/carbon black during alkali metal hydride formation would prevent the mixture of materials from sticking to both the balls and the wall of the vial. Therefore, graphite/carbon black might work as an anti-sticking agent. Another important effect was resistance of sample when contacting to air. While the composites burned on the surface

of water, they did not automatically ignite in air.

## CONCLUSIONS

Carbonaceous material mixed with zirconium hydride and alkali metal hydride had advantage to prevent materials from sticking both on the balls and the wall of the vial during preparation process. The use of graphite and carbon black also avoided burning during exposure to air and reversibility of hydrogen absorption was not deteriorated after composite formation. The higher hydrogen capacity on the zirconium-carbonaceous composite would be due to some specific sites on the carbonaceous material created during the milling.

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