Hydrogen Storage/Generating System Using Sodium Borohydride as A Hydrogen Storage Material

Sodium borohydride ($NaBH_4$), one of the highest hydrogen containing material, can serve H_2 "for a required duration", "at a required rate", and "at a required quantity", via hydrolysis of it on the unique catalyst of low-cost material. A micro hydrogen storage/generating system for the PEFC for operating mobile electronics devices using $NaBH_4$ "fuel" (hydrogen storage material) has been developed.

<Features>

(1) H_2 from the hydrolysis of sodium borohydride ($NaBH_4$), known as highest high hydrogen containing material (theoretically 10.8mass% of hydrogen generated)

(2) H_2 generated "for required duration", "at a required rate", and "at a required quantity" at room temperature under 1atm

(3) Ni-based catalyst for hydrolysis having nano-structured surface formed by uniquely developed "Fluorinating Process"

(4) Cost competitive, both sodium borohydride by a new process and catalyst by a fluorination technique

(5) Disposable sodium borohydride 'fuel" cartridge tank for compact uses – light and low-cost

(6) Sodium borohydride stored in a cartridge tank, as liquid solution or powder state

(7) Long-term operation of electronics devices by changing cartridge, without electric charge/discharge

Technologies

Hydrogen generation: large amount of H_2 generated by the hydrolysis of sodium borohydride

From 1 mole of $NaBH_4$ and 2 moles of water, 4 moles of hydrogen gas are generated. As a half of hydrogen generated are from water molecules, high hydrogen content is obtained by the special technology added. Hydrolysis can be completed under moderate conditions such as at room temperature.

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad H^o(298K) = -270kJ/mol\text{-}H_2$$

(Theoretical H-content = 10.8mass%)

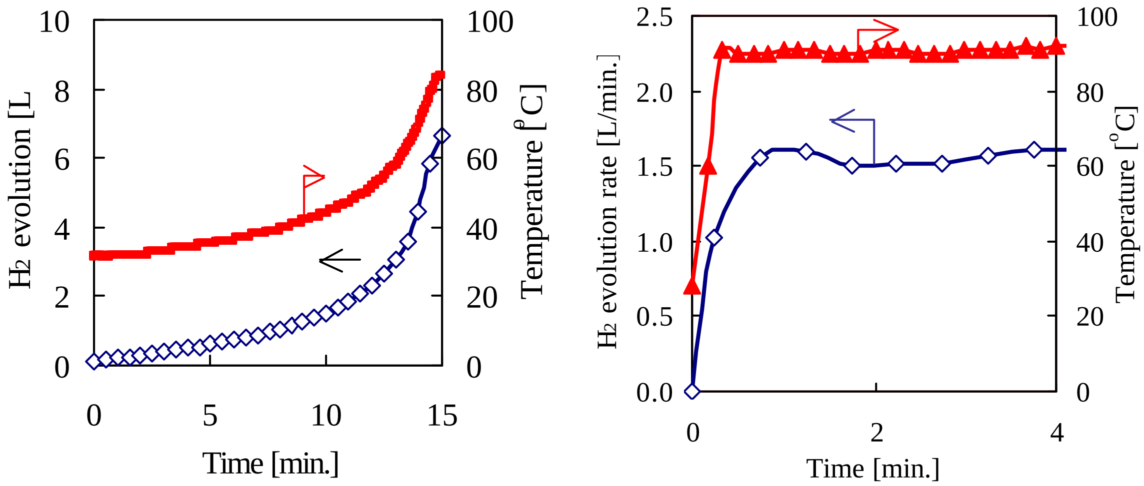
Hydrogen storage: in chemical (sodium borohydride)

Hydrogen atoms are stored in sodium borohydride as borohydride ion (BH_4^-) in an aqueous alkaline solution. The powder-state sodium borohydride can be stored in dry air permanently if otherwise in moist air. The aqueous borohydride solution can be stored in alkaline (mostly in NaOH) solution for long time.

Hydrogen generating condition: at room temperature, under 1atm, no heat source required.

- Hydrogen generating pressure: 1atm (any pressure available)
- Hydrogen generating temperature: room temperature to 100℃ (at 1atm) as required

Heat source may not be necessary under hydrogen generation, because the reaction occurs at room temperature and it is exothermic. Temperature can be higher along with the reaction proceeds, resulting much higher activity for hydrogen generation as shown below (max. 100℃ by water loss).



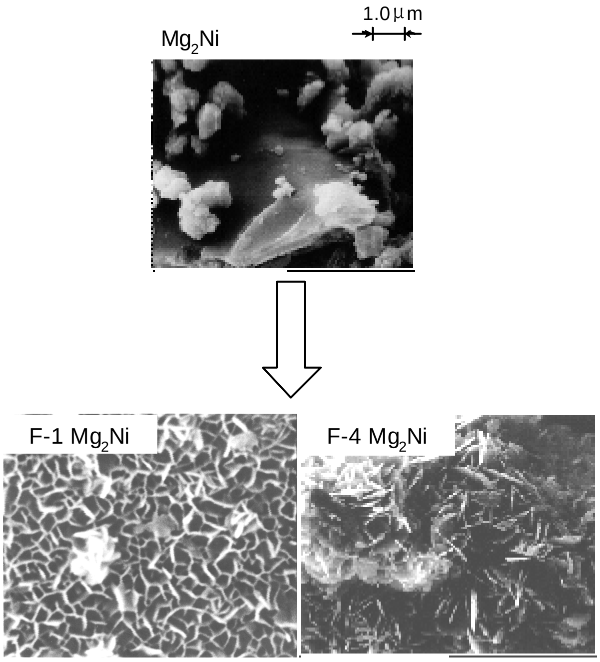
Example of enhancing hydrogen generating activity by self-heating effect

Catalyst in sodium borohydride solution (left), solution dropped on the catalyst (right)

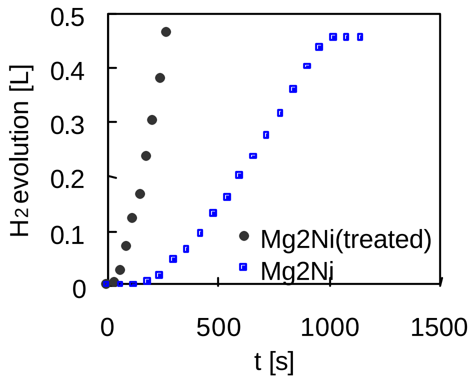
Hydrolysis catalyst: MERIT's uniquely developed Ni-base material having nano-structured surface generated by "Fluorination Process"

A unique surface treatment technology, "Fluorination Process" has been developed by MERIT and KUCEL (Kogakuin University Chemical Energy Laboratory). Catalyst for machination of carbon dioxide, anode materials for Ni-H battery and many other applications of this technology, have been developed in the past 12 years.

By Fluorination, plane surface of catalyst becomes complicated. nano-class corrugated structure covers on the surface (shown below), causing higher surface area. By high surface area and active nickel species on catalyst surface, also generated by Fluorination, the catalyst shows high reactivity for the hydrolysis of sodium borohydride.



Nano-surface structure generated by the surface treatments (Fluorination)



Enhancement of catalytic reactivity by surface treatment (Fluorination)

Safety of hydrogen storage material: almost equivalent to caustic solution.

Required consideration for health hazardous and handling of sodium borohydride is almost equivalent to caustic solution, except possibility of hydrogen evolution from the aqueous alkaline solution.

Solid byproduct of hydrogen generation (sodium metaborate, $NaBO_2$) is not harmful. Therefore required consideration of spent Fuel for safety is only that of caustic solution. A special technique for safe recovery has been filed in our patent list. Juliana

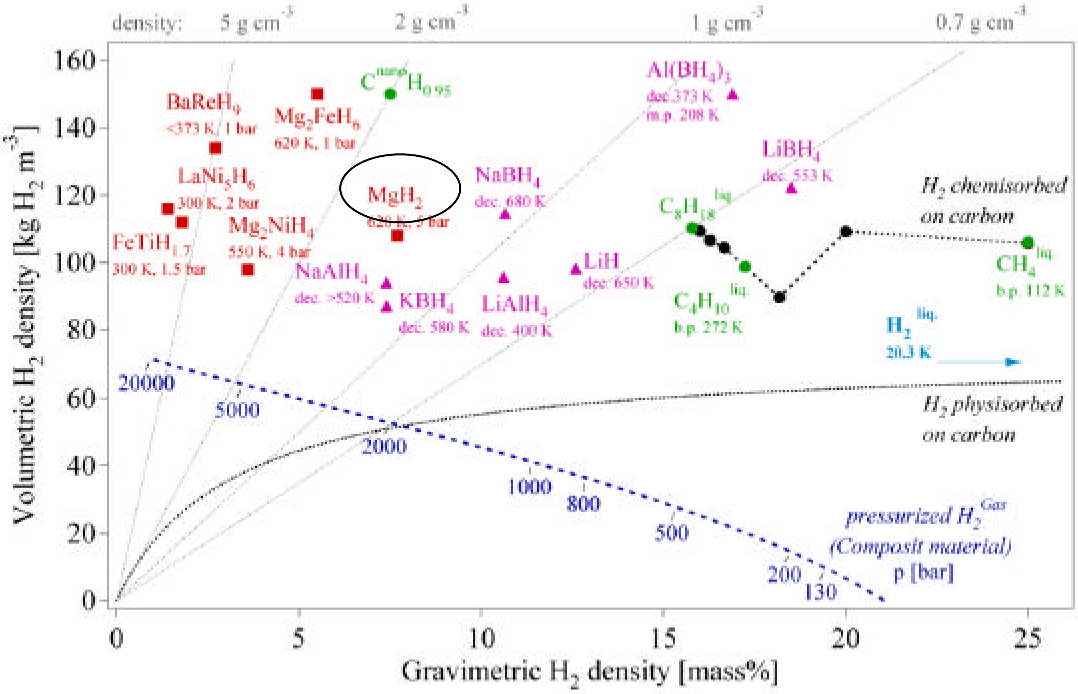
Price of materials: competitive for the "fuel" of the PEMFC for carry-in-hand electronic devices with various application technologies.

The price of sodium borohydride and the catalyst for 20W/100Wh model is approx. \$2 and \$0.03, respectively. The price of both for the fuel of the PEMFC for handy electronic devices seems enough competitive. (Note: Initial price of lithium ion battery is approx. \$600 for 100Wh)

Advantages over other technologies

A. As hydrogen storage/generating material

As shown in the figure in next page, sodium borohydride is in the group of highest hydrogen content, both weight basis and volume basis.



Original figure: by A. Zuttel and L. Sclapbach, Nature p.353, Vol. 414 (2001)

38g of sodium borohydride and 36g of water (total 74g, approx. 100cc) generate H_2 of 8g, 90L

✍✍Approx. 900atm is required to obtain same amount of H_2 by compression. H_2 compression is not suitable for mobile services by cylinder weight and safety consideration.

✍✍Several hundreds grams is required to store H_2 as metal hydrides (practical hydrogen content of 2wt%). It is also disadvantage that continuous heat input is required under hydrogen generation.

✍✍Hydrogen from natural gas or methanol by reforming requires higher temperature for reaction. It causes longer start-up duration, delay of response, care for burn injury, etc. CO, byproduct of hydrogen, should be treated to avoid poisoning of PEFC electrode and intoxication. It is also disadvantage that continuous heat input is required under hydrogen generation.

✍✍In DMFC (Direct Methanol Fuel Cell), methanol fuel is used as low concentration to avoid crossover of methanol in fuel cell, leading lower energy density or re-circulation of diluting water. Toxic of methanol should be also considered.