Sodium Silicide and Alkali Metal-Silica Gel for Convenient Hydrogen Production

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An abundant chemical resource, hydrogen has been considered as a potential energy carrier, but it has yet to meet its full commercial potential and applicability. Currently generated from nonrenewable petroleum and natural gas, hydrogen could, with an appropriate energy source, be generated from renewable resources such as water. Since hydrogen gas is exceptionally energy rich compared to gasoline on a per-weight basis, but relatively poor on a volumetric basis, large volumes of hydrogen gas must be stored and transported for direct use with the average hydrogen fuel cell. This is the brass ring to be grasped, portable hydrogen fuel cells with hydrogen generated from water. However, efficient hydrogen generation from water remains a challenging hurdle to overcome. The most daunting hurdle facing hydrogen as an energy carrier and water-based fuel cells is the need for efficient, low cost, safe, onboard hydrogen generation.

The military and a broad variety of commercial sectors, such as consumer electronics devices and stand-by power systems, are increasing their demand for advanced energy storage technologies. Hydrogen fuel cells are well suited to these wide ranging needs and are on track for replacing conventional battery systems. Yet, success in implementing small fuel cells for portable electronics applications depends largely on having a readily available hydrogen supply - one that generates, stores and/or delivers hydrogen, but in size and weight specifications for the particular application. The hydrogen fuel cell is expected to drive a digital cellular telephone for one week of talk time compared to the current five hours that lithium ion battery-powered telephones currently provide[1]. To realize this potential, a means for delivering adequate amounts of hydrogen gas to a fuel cell through a safe and easily-stored material must be developed.

Introducing SiGNa H2 Producing Powders

Sodium silicide (composition NaSi) is often considered to be so reactive that it must be labeled pyrophoric, able to spontaneously ignite in the presence of air. It has also been recently characterized as "air and moisture sensitive[2]." The reaction of NaSi with water is rapid and "violent", such that the heat of reaction can ignite the hydrogen formed, just as occurs in the reaction of alkali metals with water. This would seem to place severe restrictions on storing and handling NaSi, such as keeping it *in vacuo* or under an inert atmosphere to avoid these presumably inherent hazards.

This article describes a new simple means of instantaneous and near quantitative hydrogen generation from the chemical reduction of water with stable forms of sodium (Na) combined with silicon (NaSi) or porous oxide powders, such as silica gel (Na-SG). These stable forms are, respectively, the products of reacting crystalline silicon powder with sodium metal, or absorbing sodium into various oxide powders, such as amorphous silica gel, producing nanoparticles of NaSi within the pores. Literature precedent[3] suggests that the predominant silicide formed at 400 ºC under our conditions has the stoichiometry NaSi, with the structural unit Na_4Si_4 with four Na^+ ions surrounding a distorted tetrahedral structure $Si4^{4-}$. The powder x-ray diffraction (XRD) pattern of our material (Figure 1) shows the formation of a mixture of Na_4Si_4, unreacted silicon, and other inert products.

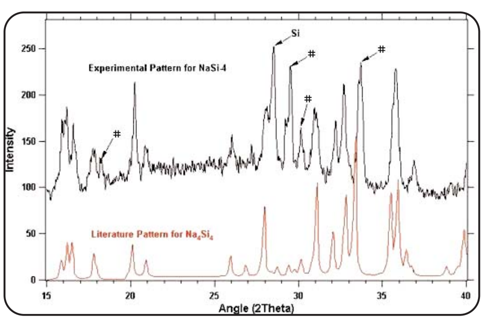

Figure 1. The X-ray powder diffraction pattern of Na4Si4, as calculated from the known crystal structure, is present in the experimental pattern. One of the peaks shows the presence of residual silicon and the four labeled with a pound signs are signature to our material.

The products are free-flowing, amorphous gray-black particles with a dull surface. The products are easily handled and used. They do not react with dry oxygen and they absorb moisture from air slowly without ignition. They react rapidly, but controllably with water to produce hydrogen. These advantageous properties combine to make these materials convenient sources for hydrogen gas, in near quantitative yield. An example of the reaction that produces the highest yield per unit mass is

$$2NaSi\ (s) + 5H_2O\ (l) \rightarrow Na_2Si_2O_5\ (aqueous) + 5H_2\uparrow + Heat\quad (\sim 350\ kJ/mol) \quad \{1\}$$

This reaction occurs rapidly and completely without a catalyst and can use any water as the hydrogen fuel source. The NaSi will not produce appreciable hydrogen gas in the absence of water. This reaction is extremely efficient on a weight basis. The reaction produces five moles of hydrogen, almost instantaneously, from the reduction of five moles of water and only two moles of NaSi. Reaction {1} is exothermic, so no energy input is needed to generate the hydrogen gas. The $Na_2Si_2O_5$ by-product is non-hazardous and easily disposed of. To generate hydrogen at the point of use, SiGNa's easily handled and dry air stable crystalline NaSi powder must simply be added to water or water must be added to it.

The hydrogen fuel stream produced from NaSi may contain small levels of impurities that do not contribute to the desired electrochemical reaction. These impurities, specifically silicon hydrides, are present in the fuel stream, but could be converted to silicon dioxide and hydrogen by a suitable reaction. For example, a small concentration of oxygen could remove the hydrides, thereby reducing fuel losses and localized heating[4]. The impurities might also be removed from the hydrogen fuel stream by increasing the yield of NaSi during particle formation, therefore removing any free silicon within the particles.

Sodium absorbed into silica gel, Na-SG, reacts cleanly with water to produce clean hydrogen that could also be utilized for smaller, transportable power systems that do not require the high efficiencies possible with NaSi. The addition of water to a sample of Na-SG rapidly produces hydrogen gas. The effect is shown in Figure 2. One gram of Na-SG produces about 170 cm^3 of H_2 at p = 1 atm and 25ºC. This material would provide a convenient, portable source of clean hydrogen upon demand, with the only gaseous products being hydrogen and water vapor. The hydrogen fuel stream could be generated at pressures greater than 3,500 psi if desired.

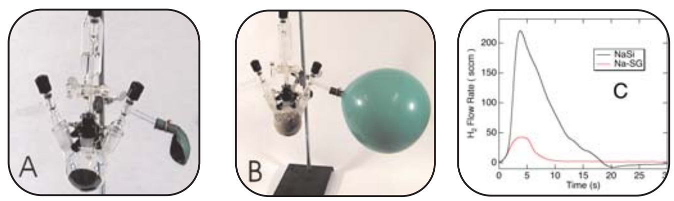

Figure 2. Reaction of water with Na-SG to produce hydrogen. (A) Before the addition of water there is a dry powder and a deflated balloon under vacuum. (B) Two minutes after addition of water the balloon is inflated. The reduced silica gel plus water is still bubbling at this stage. (C) Time dependence of hydrogen production rate from 0.1 g SiGNa powders at 30°C

SiGNa Chemistry, LLC has shown that a Na-SG-based storage system can achieve hydrogen availability equivalent to a storage density of 2.2 wt. percent H_2 by the reaction:

$$2Na\ (in\ SG)\ (s) + 2H_2O\ (l) \rightarrow H_2\uparrow + 2NaOH \quad \{2\}$$

with the evolution of about ~200 kJ of heat per mole of H_2 formed. Therefore, the reaction of Na-SG with water {2} is strongly exothermic and proceeds immediately upon the introduction to water. The Na-SG material can be prepared in a form that can be handled in air even in the presence of modest humidity levels.

Both the NaSi and the Na-SG react with water to produce H2 gas and the fuel cell produces water as a by-product, as shown in the reaction below

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O + electricity \quad \{3\}$$

The reaction to generate electricity, then, can supply/regenerate the water needed for the reaction with the NaSi or Na-SG, thus lowering the overall weight of the system. An indication of the rate of production of hydrogen from each material is given by Figure 2C. The use of both reactions in hydrogen fuel cells is currently being investigated.

Effect of Temperature on Hydrogen Evolution

Hydrogen generation efficiencies were measured for both powders, NaSi and Na-SG, by adding them to volumes of water solutions at various temperatures ranging from 30 to 60 °C. The influence of water temperature on hydrogen generation is compiled in Figure 3. The data are reported at four temperatures, measured under a N_2 blanket and upon the addition of excess water.

Upon the addition of water at all temperatures tested, the rate of evolution of hydrogen from the materials is extremely rapid, such that the hydrogen production rate may be directly controlled by the material feed rate. The data reflect a modest

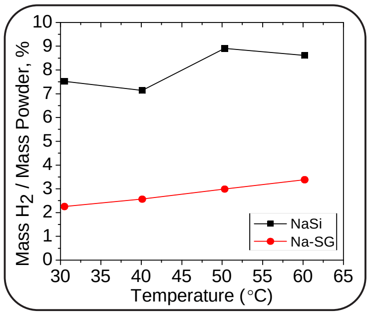

Figure 3. The effect of water temperature on the production of hydrogen fuel gas from NaSi (black) and for Na-SG (red).

effect upon temperature, with hydrogen yield increasing by ~1 percent over the 30°C temperature range shown. This may reflect the decreasing solubility of hydrogen in water as the temperature is increased. The highest yields, observed for the NaSi material, exceed 8.5 percent and approach the 9 percent target specified by the Department of Energy for its Hydrogen Storage Programs[5]. This hydrogen yield is 88 percent of the theoretical maximum as calculated from Reaction {1}. Though this yield estimate excludes the mass of required water and the balance of the plant, the exclusion of water may be justified by the onboard supply of clean product water from a downstream fuel cell. The hydrogen production and fuel cell reactions are exothermic and could provide a ready source of thermal energy for operation at temperatures above ambient.

As can be seen from the above discussion, generating H_2 from the reduction of water using NaSi or Na-SG powder has the following unique advantages:

- NaSi and Na-SG powders are stable in dry air for many months
- NaSi and Na-SG powders, as generated by our methods, are nonflammable and nonpyrophoric
- H_2 generation only occurs in the presence of water
- The only other product in the H_2 stream is water vapor, and, for NaSi, removable silicon hydrides
- H_2 generation rates are easily controlled by the rate of addition of water as liquid or vapor
- H_2 generation can occur at any temperature with liquid water
- Reaction products are environmentally safe silicates

Conclusion

Alkali metals react with water to produce hydrogen, but the metals are difficult to handle and the reactions are not easily controlled. By absorbing the metals in silica gel (porous silicon dioxide), or reacting them directly with elemental silicon, easily handled powders can be prepared that react rapidly and controllably with water to produce hydrogen. With essentially infinite shelf life in the absence of moisture, these materials could produce hydrogen in controlled amounts on demand, simply by the addition of liquid water or water vapor. The hydrogen produced could then be used to power a fuel cell. Cutting off the water supply would shut down electricity generation. Where power density per unit weight of fuel is important, the silicide, NaSi, would be the material of choice, since it can provide at least 90 grams of hydrogen per kilogram of fuel. When the power per unit weight is not critical, Na-SG could provide an easily prepared, convenient and controllable source of hydrogen that would probably not require any further purification.

References

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