

Materials Congress 2017: Si Nano powder for internal hydrogen generation materials - H. Kobayashi - Osaka University

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Si and its oxide are nonpoisonous materials, and thus, it can be taken for medical effects. We have improved a method of generation of the hydrogen by use of reactions of Si nanopowder with water in the neutral pH location. Si nanopowder is made-up by the simple bead edge method. Si nanopowder reacts with water to make hydrogen even in cases where pH is set at the neutral region between 7.0 and 8.6. The hydrogen generation rate powerfully depends on pH and in the case of pH 8.0, 55 ml/g hydrogen which reacts to that restrained in approximately 3 L saturated hydrogen-rich water is generated in 1 h. The reaction rate for hydrogen generation greatly increases with pH, show that the reacting species is hydroxide ions. The change of pH later the hydrogen stage reaction is minimal low compared with that estimated assuming that hydroxide ions are consumed by the reaction. From these results, we conclude the following reaction mechanism Si nanopowder reacts with hydroxide ions in the rate-determining response to form hydrogen molecules, SiO₂, and electrons in the conduction band. Then, created electrons are accepted by water molecules, resulting in production of hydrogen molecules and hydroxide ions. The hydrogen generation rate strongly depends on the crystallization size of Si nanopowder, but not on the size of aggregates of Si nanopowder. The present study pretense a possibility to use Si nanopowder for hydrogen phase in the body in order to necessitate hydroxyl radicals which origin various diseases.

Si nanopowder was produced from Si powder (Koujundo Chemical Laboratory Si 3 N Powder ca. 5 μm) by use of the molding milling method. Si nanopowder was fabricated using the one-step milling method with 0.5-mm diameter zirconia beads for 4 h or using the two-step milling method with 0.5-mm diameter zirconia beads for 4 h and then with 0.3-mm diameter zirconia beads for 4 h. For some specimens, etching with 5 wt% hydrofluoric acid (HF) solutions was carried out to remove a silicon oxide layer on Si nanopowder. Si nanopowder after the HF treatment was hydrophobic overdue to shallow Si-H bonds. Si nanopowder was immersed in ethanol to make the surface hydrophilic and thus to promote surface reaction with water. Si nanopowder of 10 mg with a small amount of ethanol was immersed in 30 mL water with pH adjusted between 7.0 and 8.6 by the addition of borate buffer. In a few cases, water with pH 9.0 was utilized for hydrogen generation.

The average diameters of Si crystallites for one-step and two-step milling determined from the XRD measurements are 23.4 and 13.8 nm, respectively, and the surface areas of the former and latter Si nanopowders are roughly estimated to be 110 and 190 m²/g, respectively. The ratio of the surface areas of 1.7 shows a reasonable

agreement with the ratio of the hydrogen generation rates of 1.5. This result indicates that the reactivity of Si nanopowder is determined by the Si crystallite size. It should be noted that the surface areas estimated from the size of aggregated Si nanopowders are nearly the same for one-step and two-step milling.

The specific surface areas are determined to be 74 and 143 m²/g, respectively, using the nitrogen physisorption method. The estimated specific surface areas are ~40 m²/g smaller than the surface areas determined from the average crystallite sizes. This difference may be due to the presence of micropores (i.e., <2 nm) to which nitrogen molecules cannot enter to form a second nitrogen layer (physisorbed layer). Because of the smaller size of OH⁻ ions than a part of micro pores, the ions may be able to enter them and the ratio of the effective surface areas between two-step and one-step milled Si Nano powders is likely to be smaller than the ratio of the specific surface areas determined by the BET method. As explained above, it is clearly shown that Si nanopowder reacts with water in the neutral pH region to generate hydrogen. Since Si nanopowder and its oxide are nonpoisonous, Si nanopowder can be taken to generate hydrogen in the human body. No reaction proceeds in a stomach where pH is low (pH of gastric juices: 1.5~2.0), while it reacts with OH⁻ ions in the small intestine where pancreatic juice with pH in the range between 7.5 and 8.8 is injected and also absorption efficiency is high. In the case of Si nanopowder without HF etching, a 1.6 nm silicon oxide layer is present on the nanocrystalline Si surfaces. Removal of the oxide layer by HF etching greatly increased the reaction rate, indicating that the oxide layer retarded the reaction. In fact, the calculated curve for the reaction-limited process, which curve is determined from the silicon oxide thickness, largely deviates from the experimental result shown in. On the other hand, the calculated curve for the migration-limited mechanism shown by the dotted line can well express the experimental result.

Conclusion:

We have shown that Si nanopowder reacts with water even with the neutral pH range between 7.0 and 8.6, generating hydrogen. The hydrogen generation rate greatly increases with pH, while the change of pH after the hydrogen generation reaction is negligibly low compared with that estimated assuming that OH⁻ ions are consumed for hydrogen generation. These results show that (i) the reacting species is OH⁻ ions and (ii) the concentration of OH⁻ ions remains unchanged during the hydrogen generation reaction. The unchanged pH indicates the reaction mechanism that OH⁻ ions are consumed in the initial reaction stage but electrons generated in the initial reaction stage are captured by water molecules, leading to the generation of OH⁻ ions.

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