



Activation of silicon towards hydrogen generation by pelletisation



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ABSTRACT

One of the barriers to the use of the silicon-water reaction to generate hydrogen for hydrogen fuel cells in portable devices is the lengthy induction period of the reaction caused by the presence of the native oxide layer on the surface of the silicon. Herein is presented a simple pelleting process which can be used to effectively eliminate the induction period in the reaction of pressed silicon powders with 2 wt% sodium hydroxide solution by means of disrupting the native oxide layer. The activation energy of the reaction was found to be 73 kJ/mol by means of an Arrhenius plot. It was also found that the rate of reaction of hydrogen generation could be enhanced by mixing sodium chloride and sodium polyacrylate with the silicon powder before pressing.

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1. Introduction

In recent years, the field of portable consumer electronics has blossomed [1]. The rapid rise in the functionality of such devices has put considerable strain on battery technology, which is struggling to keep up with the demand for higher power densities and longer lifetimes [2,3]. There is thus a drive to develop both better batteries and alternative technologies which could be used instead of batteries, such as hydrogen fuel cells [4,5]. Hydrogen fuel cells have several advantages over batteries (depending on the system design), including: longer lifetimes, as, in principle, as long as the hydrogen fuel cell is fed with hydrogen, it will continue to generate electricity ad infinitum as long its components function successfully, meaning that hydrogen fuel cells can deliver electricity over a substantially longer time period than batteries; a greater energy density, meaning that devices could potentially be made smaller without reducing power; independence from sources of electricity and higher chemical to electrical conversion efficiency [6–8].

However, the realization of hydrogen fuel cell-powered portable devices is very much contingent on the development of appropriate, portable sources of hydrogen. In recent years, various materials have been investigated for their suitability for portable

hydrogen generation with limited success [9–12]. The metal hydride-type materials proposed for use in vehicular applications tend to have too low an energy density for use in portable devices, and thermolysis-based hydrogen release systems typically require high temperatures which are beyond the scope of a portable device [13]. Thus hydrolysis, where chemicals are used to split water into hydrogen, has become recognized as the most promising candidate for portable applications [14–19]. Silicon has been considered as a suitable material for such systems due to its prevalent earth-abundance, high theoretical hydrogen yield of its reaction with water, formation of environmentally benign by-products and low cost [20–25]. However, we have recently shown that the gravimetric hydrogen storage density with respect to silicon is realistically far lower than the figure of 14% which is often quoted in the literature as a result of the requirement for a large excess of aqueous solution to prevent the formation of viscous byproducts which retard the rate of reaction and prevent it from going to completion [26]. A further problem with the use of silicon is that it typically exhibits a lengthy induction period in its reactions with water, to the extent that substantial quantities of an etchant, such as sodium hydroxide, invariably need to be added to generate hydrogen in useful quantities and timeframes for portable applications [27].

Previously, it has been shown that silicon can be mechanically activated towards reaction with water or basic solutions by a

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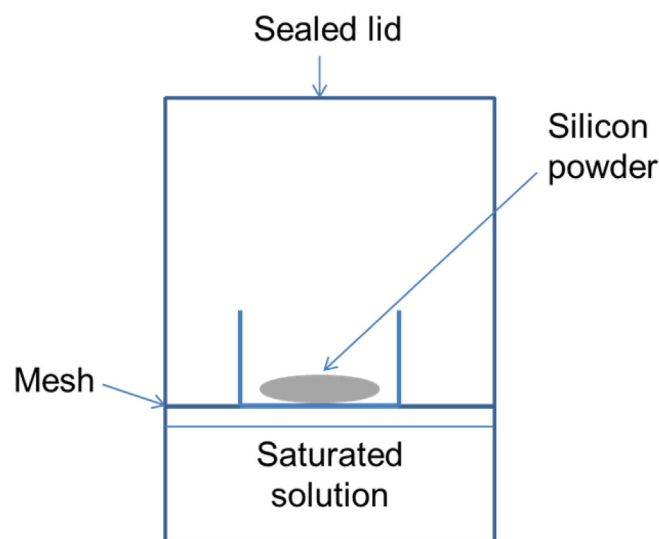
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process of ball milling [22,23]. The same authors reported that this activation can be enhanced by incorporating additives such as sodium chloride and sodium polyacrylate in the milling process. They found that these additives do not become covalently bonded to the silicon; rather, they are intimately mixed with it, and serve to activate the silicon towards hydrogen generation by either protecting it from re-passivation (i.e. by inhibiting surface oxide layer growth) or improving its dispersion into solution. Herein, in another attempt to overcome the problem of lengthy induction periods of the silicon–water reaction in the presence of hydroxide ions, we investigate the effects of a simple pelletisation method and the incorporation of different types of additive on the reaction of silicon with aqueous sodium hydroxide solutions.

2. Experimental

Silicon powder (325 mesh), sodium hydroxide, sodium chloride, magnesium nitrate and sodium polyacrylate (average M_w 5100 by GPC) were purchased from Sigma Aldrich and used as received. The as-bought silicon powder was characterized as described in Brack et al. [26]. In brief, analysis by powder X-ray diffraction showed that the silicon crystallised with the cubic Fd-3m (227) structure. X-ray photoelectron spectroscopy showed that the silicon was coated in a thin layer of silicon dioxide. The mean particle size was found to be $8.0\ \mu\text{m}$ by scanning electron microscopy. The evolution of hydrogen over time was recorded using the experimental setup described elsewhere [28]. In brief, a reaction flask was connected by a piece of tubing to a water-filled inverted measuring cylinder, which was itself placed in a beaker filled with water. The evolution of gas in the reaction flask resulted in the displacement of water from the measuring cylinder, and this water was channeled by means of a bridge into a beaker on a data-logging balance. The change in the water weight, which corresponded to the evolution of hydrogen, was measured over a period of 10 min. Pellets were prepared by mixing the desired mass of silicon powder and additive loosely together, and placing them onto the top of a 13 mm diameter anvil inserted into a die set (Specac) (Steps a–c, Scheme 1). Another 13 mm die was inserted on top (Step d, Scheme 1), and the plunger was then inserted into the die (Step e, Scheme 1). Pressure was applied using a Specac Manual Hydraulic Press (Step f, Scheme 1), and the pellets either transferred to a weighing boat or broken apart into a powder with a spatula and then reacted.

Humidity chambers ($\text{Mg}(\text{NO}_3)_2$, 52% RH at 298 K and NaCl, 75% RH at 298 K) [29] were prepared in desiccators (as shown in Scheme 2) by the addition of a solution containing the appropriate mass of magnesium nitrate or sodium chloride in deionized water to form a saturated solution and then equilibrated in an oven at 298 K. It is widely accepted that only the water vapour is mobile in humidity chambers of this design; the salt remains in the solution



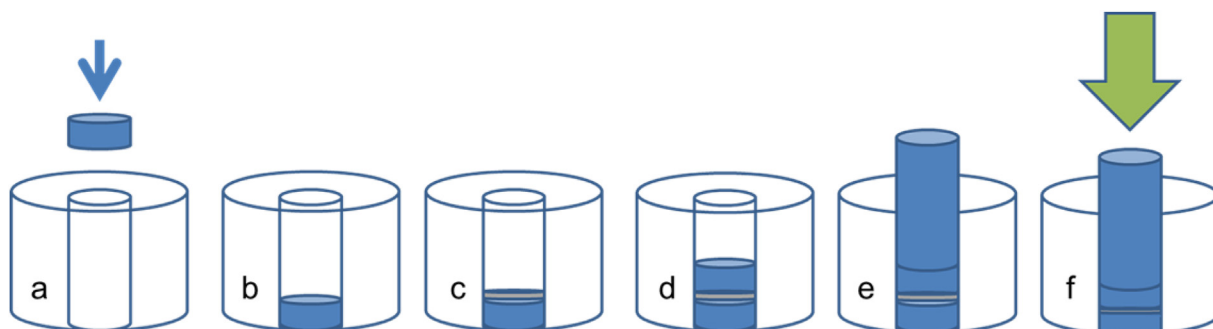
Scheme 2. A schematic of the humidity chamber set up.

well at the base of the chamber (see Scheme 2).

3. Results and discussion

Pelleting is typically considered to reduce the reactivity of substances in solution by reducing their surface area and thus their ability to react. Having in our previous work found that silicon powder required an excess of water in order to generate hydrogen in near-quantitative yields [26], it was our expectation that pressing the silicon into pellets, the most ideal form for use in a portable device, would serve to further reduce the rate of hydrogen generation. However, as can be seen from Fig. 1, though the rate of reaction was indeed retarded, it was found that the induction period was effectively eliminated, and the powders had initially, far from being passivated, in fact been activated towards hydrogen generation.

To explain this effect, two hypotheses were formulated: 1) as the reaction of silicon to form hydrogen is exothermic, the closer proximity of the reaction sites in a pellet relative to a powder may be leading to local heating effects, thus assisting in the breakdown of the oxide layer by the hydroxide ions and decreasing the induction period and accelerating the initial rate; and 2) the enhancement could be due to a disruption of the oxide layer on the surface of the silicon engendered when pressing it into a pellet. To confirm or disprove hypothesis 1), a pellet was pressed and then, rather than reacting it to form hydrogen, broken apart into a



Scheme 1. A schematic of the pellet formation process.

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