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# 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 as 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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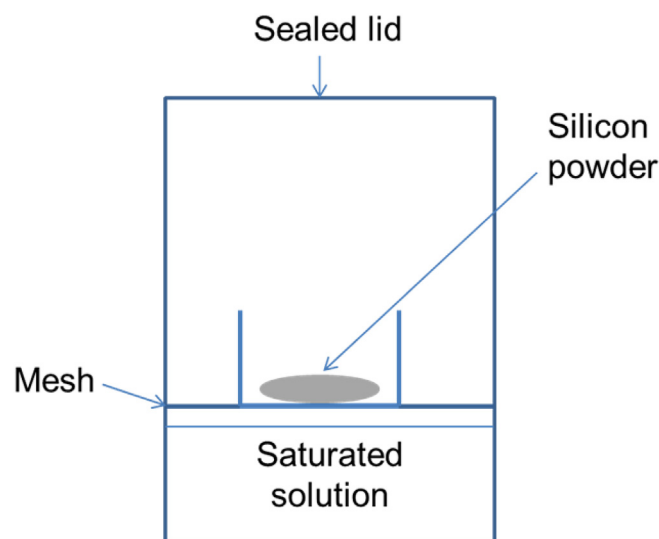
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process of ball milling [22,23]. The same authors reported that this activation can be enhanced by incorporating additives such as sodium chloride and sodium polyacrylate in the milling process. They found that these additives do not become covalently 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 repassivation (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



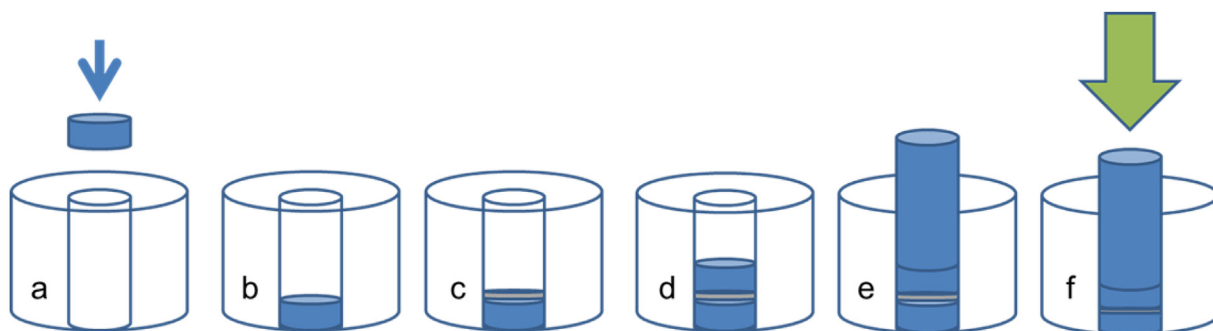
Scheme 2. A schematic of the humidity chamber set up.

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

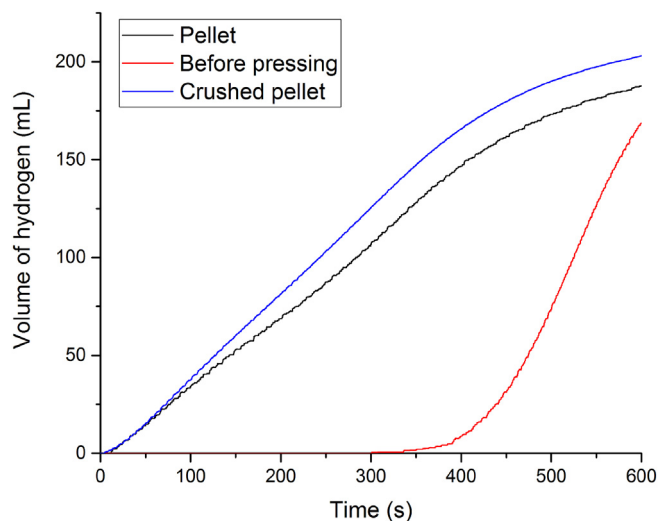
## 3. Results and discussion

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



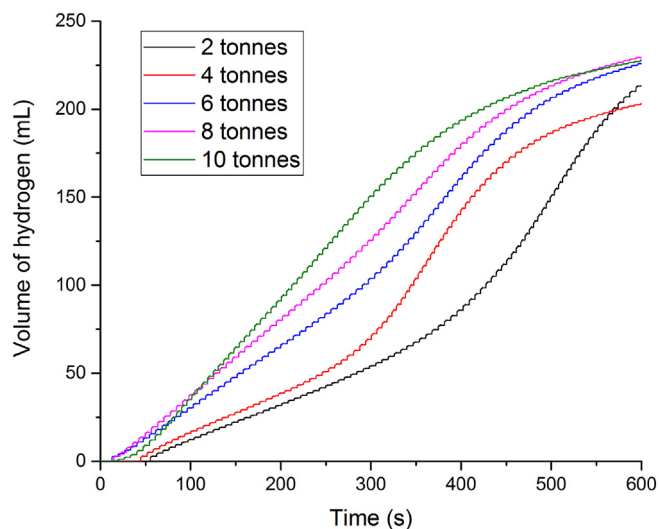
Scheme 1. A schematic of the pellet formation process.



**Fig. 1.** A comparison of hydrogen generation from the reaction of 0.2 g of silicon with 10 mL of 2 wt% sodium hydroxide solution at 50 °C. Traces are shown for as-bought silicon powder, a freshly-pressed silicon pellet and the powder obtained from breaking apart a freshly-pressed silicon pellet.

powder using a spatula (the mechanical strength of the pellets was not high and they were relatively easy to break apart). As can be seen from Fig. 1, the hydrogen generation curve of the powder obtained by breaking apart the pellet was similar to that obtained from the reaction of the pellet itself, with the powder giving a slightly enhanced rate of reaction, presumably due to its larger surface area. This suggested that hypothesis 1) was incorrect, and that the reduction of the induction period was more likely due to disruption of the oxide layer.

The effect of different pelleting pressures (Fig. 2) was also studied, reasoning that if hypothesis 2) were correct, the application of greater pressures in the pelleting process should lead to greater disruption of the oxide layer and a more pronounced effect. This was indeed found to be the case; higher pelleting pressures led to lower induction periods and more rapid initial rates of reaction. An investigation of the pressing time was also conducted (data not

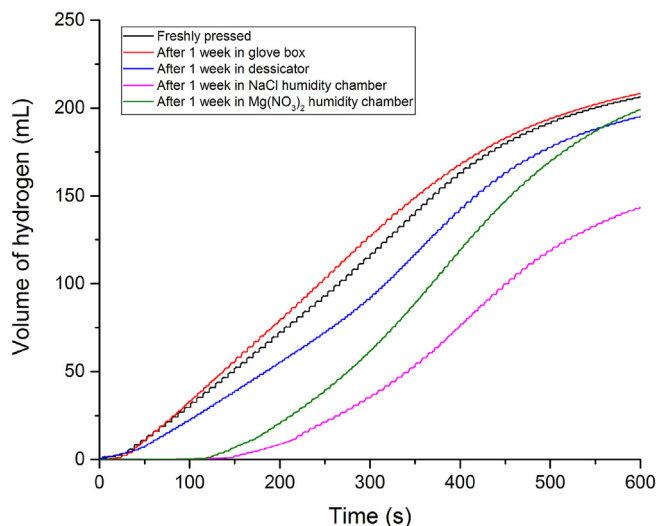


**Fig. 2.** Hydrogen generation curves from the reaction of 0.2 g of silicon powders which had previously been pressed into pellets at pressures of 2, 4, 6, 8 and 10 tonnes using a hydraulic press with 10 mL of 2 wt% sodium hydroxide solution at 50 °C.

shown), which showed that variation of the pressing time between 10 s and 10 min had no effect on the hydrogen generation properties of the obtained pellets, suggesting that the activation was entirely due to the initial pressing force applied to the powder.

In order to further confirm hypothesis 2), as it is known that the growth of silicon oxide is promoted in the presence of both air and moisture [30–34], pressed silicon powders were placed in atmospheres of varying air and moisture content, namely an argon filled glovebox, a desiccator, a humidity chamber (52% RH at 298 K) containing saturated  $\text{Mg}(\text{NO}_3)_2$  solution and a humidity chamber (75% RH at 298 K) containing saturated NaCl solution (listed in order of increasing moisture content), and the hydrogen generation properties were investigated after one week. The hydrogen generation curves are shown in Fig. 3. As would be expected if the reduction in induction period was a function of oxide layer disruption, the induction period was found to increase with increasing exposure to air and moisture. In terms of practical application, this suggests that to maintain their activation, pressed silicon powders would need to be stored in an inert atmosphere.

Having broadly established the mechanism of the activation, to provide a comparison with the literature, the effect of varying the reaction temperature was investigated in order to obtain an Arrhenius activation energy for the reaction of the pressed silicon powder with aqueous sodium hydroxide. Following convention, the initial or maximum rate of hydrogen generation (often termed the HGR) was obtained by taking the gradient of the initial, linear part of the hydrogen generation curve, where the rate of reaction is independent of the concentration of the reactants, or, in other words, the reaction follows zero-order kinetics. For a zero-order reaction (under certain assumptions), the rate of reaction (in this case, the HGR) and the rate constant,  $k$ , are equal (Equation (1)). If the rate constant and temperature of a reaction are known, the Arrhenius equation (Equation (2)) can be used to estimate its activation energy ( $E_a$ ). In the case of a zero-order reaction, the Arrhenius equation can be rewritten as shown in Equation (3), and thus the  $E_a$  of the reaction of pressed silicon powders to generate hydrogen can be estimated by a plot of  $\ln \text{HGR}$  vs.  $1/T$ , where  $T$  is temperature [35–37].



**Fig. 3.** A comparison of hydrogen generation from the reaction of 0.2 g of silicon powder with 10 mL of 2 wt% sodium hydroxide solution at 50 °C after storage for 1 week in a glove box, desiccator,  $\text{Mg}(\text{NO}_3)_2$  humidity chamber and NaCl humidity chamber. The hydrogen generation curve from a freshly pressed sample is provided for comparison.

$$\text{Rate} = k \quad (1)$$

$$\ln k = \ln A - (E_a/RT) \quad (2)$$

$$\ln \text{HGR} = \ln A - (E_a/RT) \quad (3)$$

From the Arrhenius plot (Fig. 5), the  $E_a$  for the reaction of pressed silicon with aqueous sodium hydroxide can be estimated as  $\sim 74$  kJ/mol. This is higher than for most sodium borohydride or aluminium based systems, but less than that reported for ferrosilicon [13,37–40]. Such a high  $E_a$ , indicating a wide variation of reaction rate with temperature, suggests that under these conditions, the reaction would proceed sluggishly at room temperature, which is the ideal operating temperature for portable devices.

Information concerning the nature of the transition state in the reaction can be obtained by means of an Eyring plot [35]. The Eyring equation is shown below (Equation (4)):

$$\ln \text{HGR}/T = -\Delta H^\ddagger/R \cdot 1/T + \ln(k_b/h) + \Delta S^\ddagger/R \quad (4)$$

where HGR is the hydrogen generation rate,  $\Delta H^\ddagger$  is the activation enthalpy of the reaction,  $R$  is the gas constant,  $T$  is the temperature,  $k_b$  is the Boltzmann constant,  $h$  is the Planck constant and  $\Delta S^\ddagger$  is the activation entropy of the reaction. A plot of  $\ln \text{HGR}/T$  vs.  $1/T$  will thus generate a linear plot, of which the y-intercept is equal to  $\Delta S^\ddagger/R$  and the gradient to  $\Delta H^\ddagger/R$ . Accordingly,  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  values of  $-33$  J/K/mol and  $71$  kJ/mol, respectively, were obtained for the reaction of pressed silicon with aqueous sodium hydroxide solutions (Fig. 6). A negative activation entropy indicates an associative rate-determining step. This is consistent with the literature on the etching of silicon in hydroxide solutions, in which the formation of a hydrated silicon complex by the attack of hydroxide on silicon was found to be the rate determining step [41].

In the context of ball milling, sodium chloride and sodium polyacrylate have been found to be effective additives to enhance the hydrogen generation properties of the silicon powder [22]. Specifically, and with a view to practical application, it was hoped that the addition of these additives in the pelleting process would similarly improve the rate of reaction. Thus, it was decided to investigate the effect of pressing different amounts of these additives with silicon powders.

As the mass of sodium chloride used in the pelleting process was

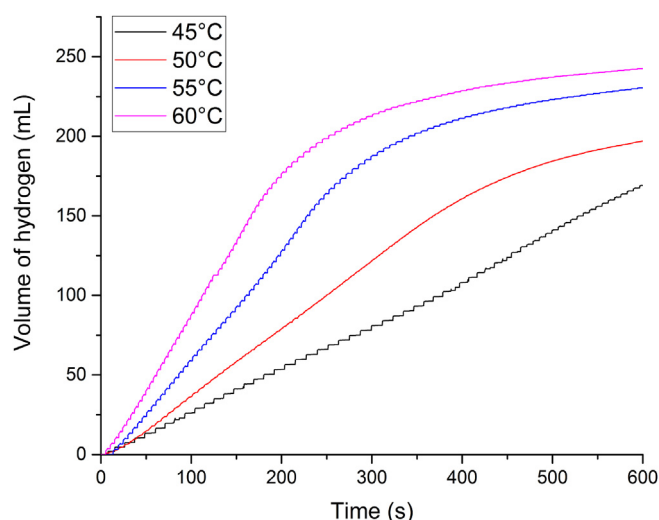


Fig. 4. Hydrogen generation curves from the reaction of 0.2 g of pressed silicon powder with 10 mL of 2 wt% sodium hydroxide solution at 45, 50, 55 and 60 °C.

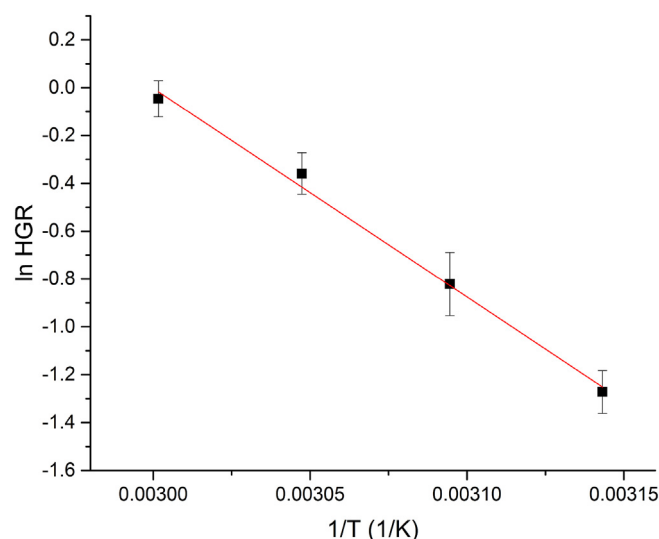


Fig. 5. An Arrhenius plot generated from the hydrogen generation curves at 45, 50, 55 and 60 °C shown in Fig. 4.

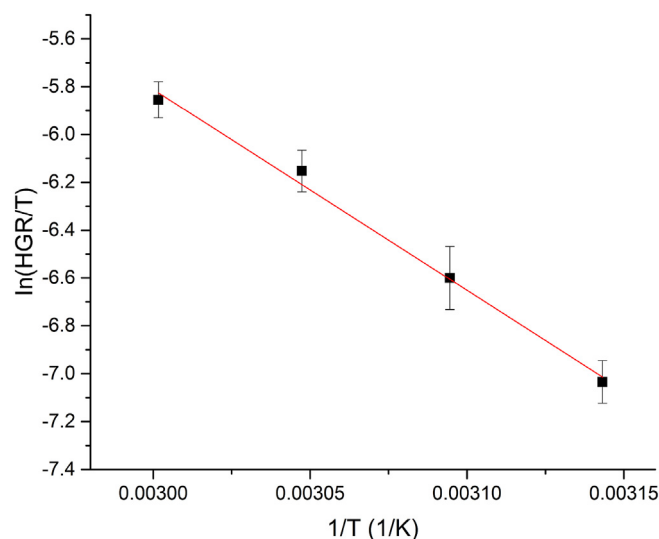
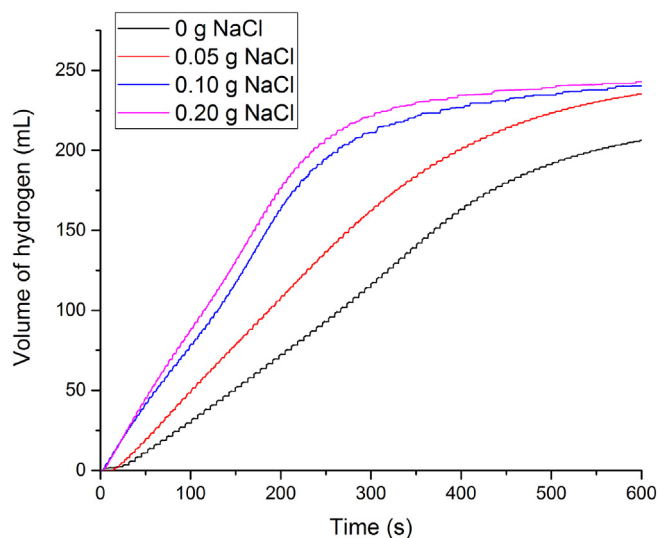


Fig. 6. An Eyring plot generated from the hydrogen generation curves at 45, 50, 55 and 60 °C shown in Fig. 4.

increased from 0 to 0.2 g (Fig. 7), the rate of reaction was found to markedly increase, though at clear cost to the gravimetric efficiency of the system. A similar activation has also been observed when ball milling aluminium with sodium chloride, and has been ascribed to disruption of the oxide layer occasioned by the creation of defects in the surface layer such as grain boundaries, inclusions and dislocations due to multiple collisions with sodium chloride particles during the milling process [42,43]. As silicon (and the native oxide layer) is substantially harder than aluminium (according to the Mohs scale) and sodium chloride, it would not be expected that it be scratched by sodium chloride if the surface oxide layer was a solid single layer rather than agglomerated as it is here. However, during the compression process, as defects formed in the native oxide layer of the silicon, the high hardness of the silicon oxide relative to the sodium chloride would lead to the generation of an intimate mixture of the two, impeding both passivation of the surface layer defects and limiting the opportunity for agglomeration of silicon particles. Sodium chloride has also been reported to





**Fig. 7.** Hydrogen generation curves from the reaction of 0.2 g of silicon powder pressed with 0, 0.05, 0.10 and 0.20 g of NaCl with 10 mL of 2 wt% sodium hydroxide solution at 50 °C.

reduce cold welding of particles during milling of aluminium, leading to a decrease in agglomerate size [44], and this may be the cause of the increase in reaction rate, which is, assuming conditions such as concentration of base, solution viscosity and solution volume remain constant, typically governed by the reactant particle size, rather than the degree of passivation. The induction period remaining negligible also fits with this explanation.

Pressing with 0.05 g of sodium polyacrylate served to increase the maximum rate of hydrogen generation (Fig. 8), though the induction period was slightly increased relative to the case with no sodium polyacrylate. The use of greater quantities of sodium polyacrylate led to further increases in induction period and a reduction in the rate of reaction. In basic solutions, silicon suspensions have a negatively charged surface, and thus interact weakly with polyanionic dispersants such as sodium polyacrylate, which is reported to be fully ionized at pH > 10 [45]. Surface adsorption of

sodium polyacrylate under such conditions is thus negligible, and the effect of sodium polyacrylate on hydrogen generation is likely to be entirely due to the action of the free sodium polyacrylate in solution. The effect of polyacrylate on the stabilisation of  $\text{Si}_3\text{N}_4$  particles (which also possess a negative surface charge in a basic environment) has previously been studied, and the following was found: 1) the stability of the dispersion was a result of electrostatic forces; and 2) the free polymer present in the system was responsible for the observed plasticity [45,46].

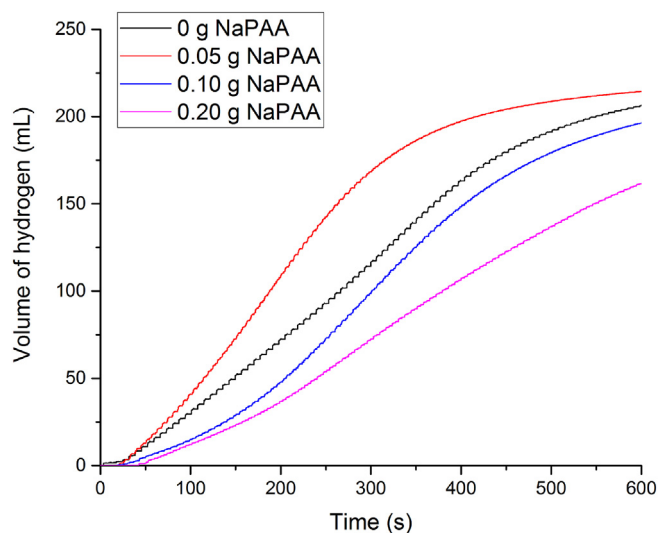
In light of this, it is suggested that the effects of pressing with sodium polyacrylate on hydrogen generation can be explained thus. As the silicon is pressed with sodium polyacrylate, an intimate mixture of silicon and sodium polyacrylate particles is formed. When this is placed into a basic solution, the sodium polyacrylate rapidly ionises and the silicon powder develops a negative charge; these similarly charged entities then mutually repel each other, leading to a more stable suspension and less agglomeration than for silicon alone and thus accounting for the increases in reaction rate (smaller agglomerate size). However, as the concentration of sodium polyacrylate is increased, the solution becomes more viscous, which may explain the decrease in reaction rate at higher concentrations of sodium polyacrylate. The increase in induction period may be explained in two ways: one is that, as sodium polyacrylate is far more adept than sodium chloride at absorbing water, it does not confer the same degree of protection from oxidation onto the activated silicon powder as sodium chloride does (in other words, water present in the sodium polyacrylate would maintain an oxidative environment in the vicinity of the freshly pressed surface), and hence an induction period remains; alternatively, it may be that higher masses of sodium polyacrylate in the intimate mixture with silicon impedes the suspension of silicon particles by producing localised high viscosity when the powder is first added to the basic aqueous solution.

#### 4. Conclusions

One of the issues with the use of the silicon-water reaction as a hydrogen generating reaction in portable hydrogen fuel cell devices is the lengthy induction periods typically exhibited due to the presence of the native oxide layer, even in the presence of moderate concentrations of etchant. Herein, a rapid, effective and simple pelleting method to reduce the induction period to negligible in the reaction of activated silicon powders with 2 wt% sodium hydroxide solution which can be accomplished with common laboratory equipment is presented. We believe that the activation stems from the disruption of the native oxide layer occasioned by pressing the silicon powder into a pellet. Though exposure to air and moisture rapidly leads to an increase in induction time, this could be counteracted by storing the powder in an inert atmosphere. Moreover, the hydrogen generation properties can be further enhanced by including appropriate amounts of cheap, non-toxic additives, namely sodium chloride and sodium polyacrylate, in the pelleting process. We believe that, if the gravimetric density can be enhanced, such a simple activation technique may have utility in the development of silicon-based composite materials for use in hydrogen generation for portable devices.

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**Fig. 8.** Hydrogen generation curves from the reaction of 0.2 g of silicon powder pressed with 0, 0.05, 0.10 and 0.20 g of NaPAA with 10 mL of 2 wt% sodium hydroxide solution at 50 °C.

## References

- [1] T. Drain, L. Grier, W. Sun, Is the growing use of electronic devices beneficial to academic performance? Results from archival data and a survey, *Issues Inf. Syst.* 13 (1) (2012) 225–231.
- [2] D. Deng, Li-ion batteries: basics, progress, and challenges, *Energy Sci. Eng.* 3 (5) (2015) 385–418.
- [3] M. Armand, J.-M. Tarascon, Building better batteries, *Nature* 451 (7179) (2008) 652–657.
- [4] J.D. Morse, Micro-fuel cell power sources, *Int. J. Energy Res.* 31 (2007) 576–602.
- [5] F. Barbir, S. Yazici, Status and development of PEM fuel cell technology, *Int. J. Energy Res.* 32 (2008) 369–378.
- [6] M.Y. El-Sharkh, N.S. Sisworahardjo, T. Yalcinoz, M.S. Alam, Portable direct hydrogen fed PEM fuel cell model and experimental verification, *Int. J. Energy Res.* 34 (2010) 643–650.
- [7] M. Winter, R.J. Brodd, What are batteries, fuel cells, and supercapacitors? *Chem. Rev.* 104 (2004) 4245–4269.
- [8] P.P. Kundu, K. Dutta, 6-Hydrogen fuel cells for portable applications, *Compend. Hydrogen Energy* (2016) 111–131, <http://dx.doi.org/10.1016/B978-1-78242-364-5.00006-3>.
- [9] D. Pukazhselvan, V. Kumar, S.K. Singh, High capacity hydrogen storage: basic aspects, new developments and milestones, *Nano Energy* 1 (4) (2012) 566–589.
- [10] A.F. Dalebrook, W. Gan, M. Grasmann, S. Moret, G. Laurenczy, Hydrogen storage: beyond conventional methods, *Chem. Commun. Camb. Engl.* 49 (78) (2013) 8735–8751.
- [11] Q.-L. Zhu, Q. Xu, Liquid organic and inorganic chemical hydrides for high-capacity hydrogen storage, *Energy & Environ. Sci.* 8 (2015) 478–512.
- [12] C. Weidenthaler, M. Felderhoff, Solid-state hydrogen storage for mobile applications: Quo Vadis? *Energy & environmental science* 4 (7) (2011) 2495.
- [13] P. Brack, S.E. Dann, K.G.U. Wijayantha, Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride (NaBH<sub>4</sub>) solutions, *Energy Sci. Eng.* 3 (3) (2015) 174–188.
- [14] G. Moussa, R. Moury, U.B. Demirci, T. Sener, P. Miele, Boron-based hydrides for chemical hydrogen storage, *Int. J. Energy Res.* 37 (2013) 825–842.
- [15] S.C. Amendola, S.L. Sharp-goldman, et al., A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst, *Int. J. Hydrogen Energy* 25 (2000) 969–975.
- [16] S. Eickhoff, C. Zhang, T. Cui, Micro fuel cell utilizing fuel cell water recovery and pneumatic valve, *J. Power Sources* 240 (2013) 1–7.
- [17] S. Eickhoff, C. Zhang, T. Cui, The effects of hydride chemistry, particle size, and void fraction on micro fuel cell performance, *J. Power Sources* 243 (2013) 562–568.
- [18] S. Moghaddam, E. Pengwang, R.I. Masel, M. Shannon, An enhanced micro-fluidic control system for improving power density of a hydride-based micro fuel cell, *J. Power Sources* 195 (7) (2010) 1866–1871.
- [19] L. Zhu, V. Swaminathan, B. Gurau, R.I. Masel, M.A. Shannon, An onboard hydrogen generation method based on hydrides and water recovery for micro-fuel cells, *J. Power Sources* 192 (2) (2009) 556–561.
- [20] N. Auner, S. Holl, Silicon as energy carrier-Facts and perspectives, *Energy* 31 (10–11) (2006) 1395–1402.
- [21] F. Erogbogbo, T. Lin, et al., On-demand hydrogen generation using nano-silicon: splitting water without light, heat, or electricity, *Nano Lett.* 13 (2) (2013) 451–456.
- [22] Foord, J. S. & Hu, J. Composition for hydrogen generation. WO2014053799, UK, 10.04.2014.
- [23] Foord, J. S. & Ashraf, S. Preparation of silicon for fast generation of hydrogen through reaction with water. WO2011058317, UK, 10.05.2011.
- [24] Y. Hu, H. Yan, K. Liu, H. Cao, W. Li, Hydrogen production using solar grade wasted silicon, *Int. J. Hydrogen Energy* 40 (28) (2015) 8633–8641.
- [25] T.-L. Kao, W.-H. Huang, H.-Y. Tuan, Kerf loss silicon as a cost-effective, high-efficiency, and convenient energy carrier: additive-mediated rapid hydrogen production and integrated systems for electricity generation and hydrogen storage, *J. Mater. Chem. A* 00 (2016) 1–8.
- [26] P. Brack, S.E. Dann, K.G.U. Wijayantha, P. Adcock, S. Foster, An assessment of the viability of hydrogen generation from the reaction of silicon powder and sodium hydroxide solution for portable applications, *Int. J. Energy Res.* (2016), <http://dx.doi.org/10.1002/er.3604>.
- [27] E.D. Palik, H.F. Gray, P.B.A. Klein, Raman study of etching silicon in aqueous KOH, *J. Electrochem. Soc.* 130 (4) (1983) 956–959.
- [28] P. Brack, S.E. Dann, K.G.U. Wijayantha, P. Adcock, S. Foster, A simple, low-cost, and robust system to measure the volume of hydrogen evolved by chemical reactions with aqueous solutions, *J. Vis. Exp.* 114 (2016) e54383, <http://dx.doi.org/10.3791/54383>.
- [29] L.B. Rockland, Saturated salt solutions for static control of relative humidity between 5 and 40 °C, *Anal. Chem.* 32 (10) (1960) 1375–1376.
- [30] G.F. Cerofolini, L. Meda, Mechanisms and kinetics of room-temperature silicon oxidation, *J. Non Cryst. Solids* 216 (1997) 140–147.
- [31] M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, M. Ohwada, Growth of native oxide on a silicon surface, *J. Appl. Phys.* 68 (3) (1990) 1272–1281.
- [32] T.A. Miura, M. Niwano, D. Shoji, N. Miyamoto, Initial stages of oxidation of hydrogen-terminated Si surface stored in air, *Appl. Surf. Sci.* 100–101 (1996) 454–459.
- [33] G.F. Cerofolini, D. Mascolo, M.O. Vlad, A model for oxidation kinetics in air at room temperature of hydrogen-terminated (1 0 0) Si, *J. Appl. Phys.* 100 (5) (2006) 0–11.
- [34] J. Salonen, V.-P. Lehto, E. Laine, The room temperature oxidation of porous silicon, *Appl. Surf. Sci.* 120 (3–4) (1997) 191–198.
- [35] J. Zhu, R. Li, W. Niu, Y. Wu, X. Gou, Facile hydrogen generation using colloidal carbon supported cobalt to catalyze hydrolysis of sodium borohydride, *J. Power Sources* 211 (2012) 33–39.
- [36] J. Zhu, R. Li, W. Niu, Y. Wu, X. Gou, Fast hydrogen generation from NaBH<sub>4</sub> hydrolysis catalyzed by carbon aerogels supported cobalt nanoparticles, *Int. J. Hydrogen Energy* 38 (25) (2013) 10864–10870.
- [37] P. Brack, S.E. Dann, K.G.U. Wijayantha, P. Adcock, S. Foster, An old solution to a new problem? Hydrogen generation by the reaction of ferrosilicon with aqueous sodium hydroxide solutions, *Energy Sci. Eng.* 3 (6) (2015) 535–540.
- [38] R. Retnamma, A.Q. Novais, C.M. Rangel, Kinetics of hydrolysis of sodium borohydride for hydrogen production in fuel cell applications: a review, *Int. J. Hydrogen Energy* 36 (2011) 9772–9790.
- [39] M.Q. Fan, S. Liu, C. Wang, D. Chen, K.Y. Shu, Hydrolytic hydrogen generation using milled aluminum in water activated by Li, in, and Zn additives, *Fuel Cells* 12 (4) (2012) 642–648.
- [40] V. Rosenband, A. Gany, Application of activated aluminum powder for generation of hydrogen from water, *Int. J. Hydrogen Energy* 35 (20) (2010) 10898–10904.
- [41] H. Seidel, L. Csepregi, A. Heuberger, H. Baumgartel, Anisotropic etching of crystalline silicon in alkaline solutions, *J. Electrochem. Soc.* 137 (11) (1990) 3612–3626.
- [42] N. Kumar Ashvin Swamy, E. Shafirovich, Conversion of aluminum foil to powders that react and burn with water, *Combust. flame* 161 (2014) 322–331.
- [43] K. Mahmoodi, B. Alinejad, Enhancement of hydrogen generation rate in reaction of aluminum with water, *Int. J. Hydrogen Energy* 35 (11) (2010) 5227–5232.
- [44] X. Chen, Z. Zhao, M. Hao, D. Wang, Research of hydrogen generation by the reaction of Al-based materials with water, *J. Power Sources* 222 (2013) 188–195.
- [45] V. Hackley, A colloidal processing of silicon nitride with poly(acrylic acid): II, rheological properties, *J. Am. Ceram. Soc.* 81 (9) (1998) 2421–2428.
- [46] V.A. Hackley, U. Pa, B. Kim, S.G. Malghan, Aqueous processing of sintered reaction-bonded silicon nitride: I, dispersion properties of silicon powder, *J. Am. Ceram. Soc.* 80 (1997) 1781–1788.