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Silicon as an intermediary between renewable energy and hydrogen

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May 5, 2004

No. 11

Research Notes

Working Paper Series

Silicon as an intermediary between renewable energy and hydrogen

- Global reserves of coal, oil and natural gas are diminishing; global energy requirements however are dramatically increasing. Renewable energy sources lower the threat to the earth's climate but are not able to meet the energy consumption in major urban areas. The opinion of many experts is that the future will be dominated by hydrogen. However, this gas is essentially totally manufactured from fossil fuels and is hence of limited abundance – not to mention the hazards involved in its utilisation.
- A novel energy concept involving solar and thus carbon-independent hydrogen-based technology necessitates an intermediate storage vehicle for renewable energy. This future energy carrier should be simple to manufacture, be available to an unlimited degree or at least be suitable for recycling, be able to store and transport the energy without hazards, demonstrate a high energy density and release no carbon dioxide or other climatically detrimental substances.
- Silicon successfully functions as a tailor-made intermediate linking decentrally operating renewable energy-generation technology with equally decentrally organised hydrogen-based infrastructure at any location of choice. In contrast to oil and in particular hydrogen, the transport and storage of silicon are free from potential hazards and require a simple infrastructure similar to that needed for coal.



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Non-renewable energy sources are becoming depleted. Air and water (our environment) are precious and will be under increased jeopardy without effective energy and environmental policies. A hydrogen technology based upon solar energy represents a viable solution to these problems. With this scientific paper, Deutsche Bank Research wishes to simultaneously provide a platform and a warning for the debate which in all honesty is not really taking place. We are grateful to Professor Auner for his research activities in this extremely important area and also for his objective of utilising these results and findings so that their benefits are not limited to those currently in possession of energy.

Norbert Walter

Silicon as an intermediary between renewable energy and hydrogen

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Main

Global reserves of coal, oil and natural gas are decreasing drastically; global energy requirements however are dramatically increasing. Energy generation using nuclear technology could possibly become abandoned and regenerative energy sources are not able to meet energy consumption in major urban areas. The future lies with hydrogen. However, this gas is essentially totally manufactured from fossil fuels, and hence is of limited abundance – not to mention the dangers involved in its utilisation. A new approach to solve the energy problem is being sought. Silicon instead of coal and oil, could this be the answer?

The current situation: motivation to develop the present concept

Our present energy generation concepts are essentially based on carbon (crude oil, natural gas) as a source of raw materials.¹ The resulting energy supply process consequently produces the greenhouse gas carbon dioxide, CO₂. Scientific studies prove that the natural carbon-based resources are becoming dramatically exhausted: “Mankind consumes more carbon-based energy per day than was formed in a thousand years of the earth’s history”. Furthermore, it is expected that energy consumption will double in the next forty years.^{2a}

The reasons for this can be traced back to the expected increase in the world population (currently in excess of 6 billion with prognoses for 2060 of around 10 billion), activities to reduce shortfalls in third world

countries, along with technological developments particularly in Asia.

Recent calculations suggest that the global reserves of oil will last for about 42 years, those of natural gas are estimated to suffice for 60 years and coal is estimated to be available for about 250 years.^{1,3} To summarise, there is no doubt that the reserves are finite. Oil and natural gas will become less available as energy sources become scarce and consequently more expensive.

Taking into consideration the rephrasing discussions aimed at effecting a reduction in CO₂ emission, it is extremely apparent that the search for and development of alternative energy sources are of eminent importance.

One possible approach to this problem is the employment of so-called renewable energy. Biomass, wind, hydroelectric and solar power will certainly be utilised where the geographic and climatic prerequisites are favourable. Unfortunately, regions exhibiting preferential conditions do not usually coincide with the areas of high energy consumption, such as industrial nations with a high population density. Furthermore, those regions particularly suitable for the generation of large capacities of renewable energy seldom have access to the economic and technological infrastructures necessary to store or transport the energy.^{4,5} This raises the logical question of finding an efficient secondary energy-carrying vehicle enabling permanent energy storage and safe energy transportation, since direct transport of primary electrical energy via long-distance high-voltage power lines is prone to considerable energy losses. Furthermore, electric energy cannot be effectively stored and therefore necessitates immediate use by consumers. According to numerous experts, this future energy-carrying vehicle will be hydrogen, which produces water as the result of the highly efficient energy-delivering combustion process.^{2,6} In spite of huge investments, however, the hydrogen-based energy concept is still controversial, and rightly so:

- (i) Hydrogen is currently manufactured using crude oil or natural gas.⁷ Without these raw materials, there is no hydrogen.
- (ii) Water can be used as an alternative hydrogen source: Using considerable amounts of energy, it is split into hydrogen and oxygen which are subsequently recombined to generate water and energy – possibly involving expensive and hazardous handling during the transport and storage of the hydrogen. The problem is that large areas of our globe are lacking water! Other hydrogen sources, such as metal hydrides, are less efficient.
- (iii) The energy input necessary to generate hydrogen from water is immense (286 kJ/mol compared to 37.5 kJ/mol for natural gas (methane)). The thermodynamically most efficient source material for hydrogen generation is ammonia; to decompose this into hydrogen and nitrogen, only 30.8 kJ/mol is required, i.e. approx. 10% of the energy as necessary for water decomposition.^{7,8} The Haber-Bosch process for the synthesis of ammonia requires high inputs of energy and exhibits low product yields from the hydrogen and nitrogen starting materials.⁷ Once again, the hydrogen consumed in that process is based upon hydrocarbons which, as previously discussed, renders the use of ammonia unrealistic as a source of hydrogen due to the dependence upon carbon.
- (iv) The generation, storage and transport of liquid or gaseous hydrogen involves enormous expenditure of energy (condensation requires roughly 1/5 of the heat of combustion) and the diffusion behaviour is difficult to control, further enhancing the hazard potential. Many experts therefore consider a “hydrogen age” unrealistic in view of the enormous costs involved, unless this energy-bearing gas can be generated close to the consumer from a suitable source medium and is used immediately to generate energy (decentral energy supply).
- The technical feasibility of large-scale activities involving hydrogen thus require the use of an intermediate storage medium for regenerative energy. This future energy carrier which unlike the fossil fuels is not naturally available must meet specific requirements. It should:
- (i) be simple to synthesise using, when possible, regenerative energy sources,
 - (ii) be available to an unlimited degree or at least be suitable for recycling,
 - (iii) be transportable without hazard and be capable of permanent energy storage,
 - (iv) demonstrate a high energy density,
 - (v) release no carbon dioxide in high-tech population centres and,
 - (vi) supply valuable combustion products, if possible.
- In other words, we are seeking a medium which is capable of decentrally producing ammonia or hydrogen without the involvement of carbon or carbon dioxide.
- These pre-requirements can be met using three materials: silicon, water and air, where silicon is the energy carrier.
- Silicon: description, availability and reactivity**
- Approximately 75% of the accessible earth’s crust comprises silicon dioxide, SiO₂ (Si: 26.3%; O₂: 48.9%).^{7,9}
- Today, quartz sand (SiO₂) is converted into crystalline silicon on a megatonne scale (1.2 million tonnes Si in 2000) by reduction with carbon using an electric arc process (T ~ 2000° C). The process has considerable energy requirements (12,000 kWh/t silicon; technically realised energy efficiency: 84%) and significant volumes of CO₂ are released.

Based upon fossil-reducing agents this amounts to 4.3 t CO₂/t silicon but this can be lowered to 1.8 t CO₂ using biological carbon sources (charcoal). The electrical energy required for heating purposes is generated hydroelectrically or atomically. The use of natural gas or oil to generate electricity increases the CO₂ emissions to 10.6 and 17.7 t CO₂/t silicon respectively.^{10,11}

An electrochemical production under electrolytic conditions involving reduced levels of carbon and hence CO₂ has been verified in pilot projects; however, large-scale operations have not yet been implemented because of commercial considerations.¹⁰

A chemical process that enables a completely carbon-independent production of silicon makes use of the resources “sand” and inexpensive excess energy – ideally renewable forms – to manufacture silicon and thus act as an energy storage medium.

Beginning with conventional desert or sea sand which contains approximately 80 - 90% α-quartz, silicon is obtained using technologically well established, large-scale processes as a high purity powder with no byproducts.¹²

This process is not in competition with the current silicon production via electric arc ovens; however, it could certainly develop into an attractive alternative as an option to permit the manufacture of high-purity (electronic) silicon in a future with depleted carbon reserves. The cycle remains completely free of C/CO₂ and no by-products are generated. The sole starting material is sand which, in contrast to the present-day technology, can even be low-quality grades. The complementary result of our basic research activities is a second technical process which effectively thermally converts silicon tetrahalogenides to silicon in a gas phase reaction.^{13,14} This simplifies the manufacture of silicon to an analog of the so-called Siemens process that is currently employed to produce electronic-grade silicon from chlorinated silicon compounds.¹⁵ It has been possible to directly generate the

secondary energy carrier silicon from desert sand on a laboratory scale in a two-stage process using solar energy. Of course, studies to transfer this to a large-scale operation are now necessary.

The reactivity of silicon can be influenced by the selection of reaction conditions in the manufacturing process to match the application requirements: hard metallic fragments of low reactivity (i.e. highly stable during transportation and storage) can be manufactured as can black powder products of large surface areas which can be highly reactive. This can be observed in the conversion of the black powder substance into silicon dioxide (SiO₂) by simple air oxidation at room temperature. The oxidation of silicon is dependent upon temperature as illustrated in Figure 1. This demonstrates the oxidation of four different silicon samples and correlates very impressively with Figure 2, which illustrates a highly reactive silicon powder sample that spontaneously ignites upon contact with air.

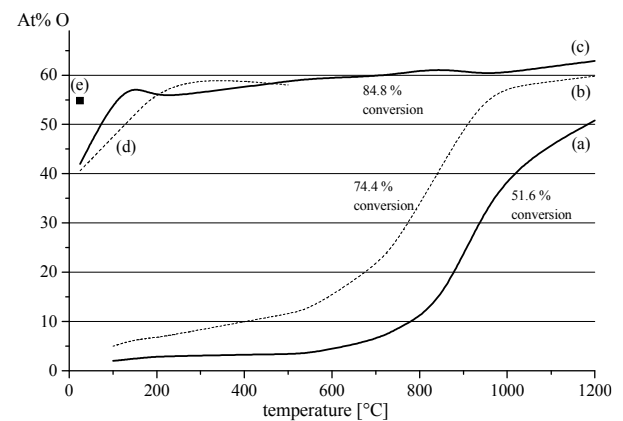


Figure 1: Oxidation of various Si samples with air as a function of temperature: (a) metallic silicon, particle size 1 – 70 μm; (b) amorphous silicon produced by the reduction of SiO₂ by magnesium at elevated temperatures; (c) to (e) various amorphous Si samples where sample (e) is almost completely oxidised after 5 days at room temperature.

The energy required to convert sand into silicon is essentially stored in the energy carrier manufactured in this way and which additionally fulfils all the previously listed criteria. The carrier is a permanent storage

medium for the energy and can be transported conventionally in environmentally compatible fashion (the high reactivity of amorphous silicon as described above is of course deliberately reduced first of all by specific occupation of surface sites or thermally induced crystallisation). The stored energy can easily be released by a simple oxidation reaction under relatively mild and controllable conditions.

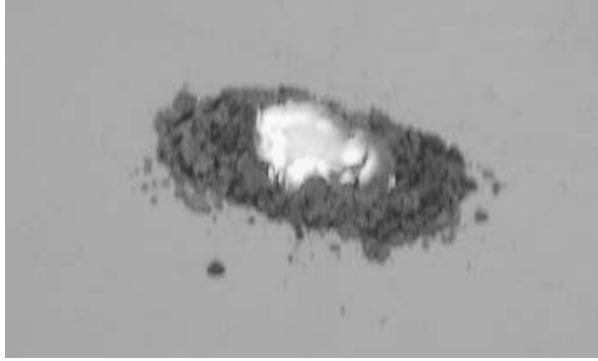


Figure 2: *Highly reactive silicon powder that spontaneously ignites upon contact with air.*

Silicon as an energy carrier – valuable combustion products

The reduction process $\text{sand} \rightarrow \text{silicon}$ generates a permanent energy carrier with an energy density and energy content comparable with that of carbon: silicon is equally as good as carbon and the natural resources are unlimited (Table 1).¹⁶

	Carbon	Silicon
Energy content [kJ/g]	32.8	32.6
Energy density [kJ/cm ³]	74.2	75.9

Table 1: Comparison between the energy carriers carbon and silicon.

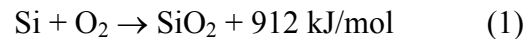
It is well known that conventional metallic silicon reacts exothermally with oxygen only at high temperatures ($T > 1500^\circ\text{C}$, Fig. 1) to completely give silicon dioxide and heat (eq. 1). The thermal energy released, which is about 9 kWh/kg Si,^{10,16} then can be transformed into electric energy using conventional technology. Taking into consideration the overall energy needed for the production of silicon ($\sim 12 \text{ kWh/kg Si}^{10}$),

the storage efficiency factor lies at almost 30% and is thus comparable with the system:

water \rightarrow hydrogen (electrolysis) \rightarrow water

assuming a constant conversion factor of 0.391 for the transformation of thermal energy into electrical energy in industrial power plants.¹⁷

Silicon offers an additional advantage over carbon: silicon can be combusted under a nitrogen atmosphere to give silicon nitride (eq. 2) as opposed to the silicon dioxide which is formed on combustion with oxygen (eq. 1). At temperatures above 1100°C and with iron catalysts, this reaction can be used to manufacture Si_3N_4 , a highly valuable and robust material. Based on this reaction scheme, air ($\sim 80\% \text{ N}_2$, $20\% \text{ O}_2$) would become the ideal reaction partner for silicon to produce thermal energy and highly valuable ceramic materials as solid combustion products. But how can silicon be activated to react with air according to the following equations (1) and (2)?



The answer to this question has already been provided.¹⁸

With a copper oxide catalyst, metallic silicon powder reacts with nitrogen under relatively mild conditions ($\sim 600^\circ\text{C}$) to give silicon nitride, a chemically and physically resistant ceramic material.

The products of the highly efficient combustion reactions given in equations (1) and (2) are pyrogenous or high-disperse silica (sand) and silicon nitride. These can be utilized further: synthetic silica are employed as base materials in the manufacture of insulation and construction materials, as fillers for rubbers, as carriers for agricultural products, as flow agents and inert additives.¹⁹ Based on its stability to temperature changes and corrosion as well as its physical strength, silicon nitride is used as a hardening treatment

for gas tubes (e.g. for chlorine), casting dies and fittings, pump components, cutting tools, turbine components etc.¹⁹

Upon reaction with steam or bases, silicon nitride releases ammonia.²⁰ Apart from “sand”, further products of this reaction include metal silicates which can be used in the production of glass materials. Ammonia can be directly employed as a base material for fertilisers (production: 120 million tonnes per year⁷), as a fuel or as an energy-efficient source of hydrogen.

This means: energy suitable for a variety of purposes can be generated from silicon, water and air along with interesting by-products including material and fertilisers, ammonia, and hydrogen.

Silicon as an energy carrier – a safe source of hydrogen

In simple chemical processes, silicon nitride reacts at approx. 350° C with bases, or at higher reaction temperatures (~ 1000° C) even with water vapour to produce silicates, sand, and ammonia (eq. 3, Fig. 3).²⁰



Ammonia is the most thermodynamically favourable source for hydrogen (along with nitrogen; retro Haber-Bosch process).¹⁵ Whereas 18.75 kJ are necessary to produce 1 g of hydrogen from methane, water and ammonia require 143 kJ and 15.4 kJ respectively.^{7,8} Correspondingly, the ratio of the energy requirement to generate hydrogen from water and ammonia is 9.3/1.

Figure 3 describes the formation of ammonia following the reaction of silicon nitride with water as a function of time and using soda (Na_2CO_3) as a carrier for the nitride. The soda decomposes at temperatures in excess of 770° C leading to sodium oxide. This forms sodium hydroxide in the presence of water which in turn is responsible for the quantitative formation of ammonia at high reaction temperatures.²⁰

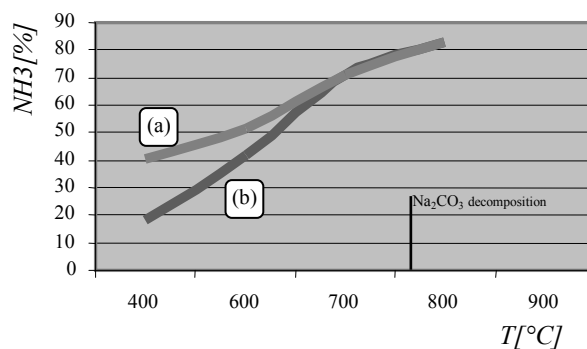


Figure 3: Release of ammonia from silicon nitride. (a) low concentration of silicon nitride; (b) high concentration of silicon nitride.

The thermal decomposition of ammonia without catalyst is shown in Figure 4. The curve (a) indicates how the decomposition increases proportionally with temperature. It begins at temperatures of about 300° C with the formation of hydrazine (b), which itself decomposes above 1000° C to nitrogen and hydrogen (c).²¹ The decomposition temperature can be effectively reduced by up to 300 – 400° C using transition metal catalysts.²²

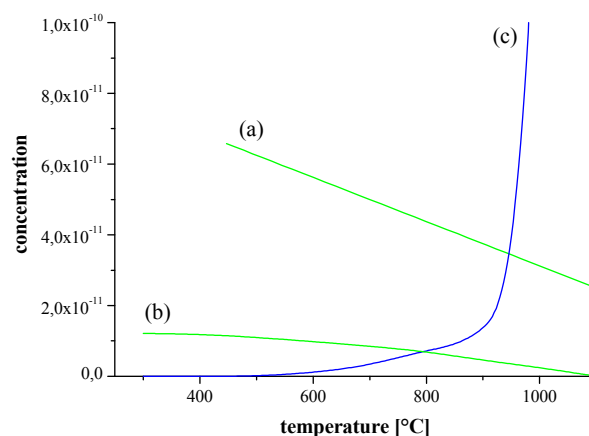
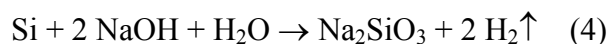


Figure 4: Temperature dependency in the formation of hydrogen from ammonia: (a) thermal decomposition of ammonia with increasing temperature; (b) formation and decomposition of hydrazine with increasing temperature; (c) temperature-dependent generation of hydrogen from ammonia.

A reaction mechanism involving ammonia as an intermediate product is not absolutely necessary in the production of hydrogen from silicon. Literature references have been cited where metallic silicon reacts directly with water to form silicates and hydrogen for example under alkaline conditions (eq. 4).²³



This is not an unexpected reaction since all metals and metal hydrides of Group I–IV elements exhibit this property.

However to guarantee the technical feasibility of the reaction, the following conditions must be fulfilled:

- relative to the volume of hydrogen generated, the weight of metal must be as low as possible
- no further materials other than water should be consumed
- apart from hydrogen the product of the reaction should be anhydrous metal oxides.

Table 2 provides a comparison of the theoretical energy densities of metals and metal hydrides which release hydrogen in aqueous solution. The figures indicate the minimum heating capacity of the evolved hydrogen at complete material conversion.²⁴

The following conclusions can be derived from this list of energy densities and the chemical properties of these potential hydrogen sources: Despite high energy densities in some cases, alkali metals and/or their hydrides are not utilised to generate hydrogen as they must be stored and transported under exclusion of air. Furthermore, the metals are very often rarely occurring.²⁵ The alkaline earth metal beryllium appears to be ideally suited for the generation of hydrogen; however, it is highly toxic and extremely rare, both of which exclude it from large scale applications.²⁶ Based upon natural occurrence, reactivity and energy density, magnesium represents an interesting candidate for hydrogen generation; however, the equivalence in appropriate properties renders aluminium,²⁷ zinc,²⁸ and silicon more attractive. Special consideration should also be given to alkaline borates²⁹ and alkaline aluminates²⁹ that have proven unsuitable for large-scale application because of the complexity of their syntheses and the high costs associated with these. They do

Material	Reaction mechanism leading to hydrogen formation	Energy density relative to		
		Starting product [MJ/kg]	Final product [MJ/kg]	Average [MJ/kg]
Li	$\text{Li} + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{LiOH} + \frac{1}{2} \text{H}_2$	17.1	5.0	11.0
Na	$\text{Na} + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2} \text{H}_2$	5.2	3.0	4.1
Be	$\text{Be} + 2 \text{H}_2\text{O} \rightarrow \text{Be}(\text{OH})_2 + \text{H}_2$	26.7	5.6	16.1
Mg	$\text{Mg} + 2 \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{H}_2$	9.9	4.1	7.0
Ca	$\text{Ca} + 2 \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{H}_2$	6.0	3.2	4.6
Al	$\text{Al} + 3 \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \frac{3}{2} \text{H}_2$	13.3	4.6	9.0
Si	$\text{Si} + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2 \text{H}_2$	17.1	8.0	12.6
Fe	$\text{Fe} + \frac{4}{3} \text{H}_2\text{O} \rightarrow \frac{1}{3} \text{Fe}_3\text{O}_4 + \frac{4}{3} \text{H}_2$	5.7	4.2	4.9
Zn	$\text{Zn} + 4 \text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_4 + 2 \text{H}_2$	7.3	3.6	5.5
LiH	$\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$	30.4	10.0	20.0
NaH	$\text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$	10.0	6.0	8.0
CaH ₂	$\text{CaH}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2 \text{H}_2$	11.4	6.5	9.0
NaBH ₄	$\text{NaBH}_4 + 2 \text{H}_2\text{O} \rightarrow 4 \text{H}_2 + \text{NaBO}_2$	25.4	14.6	20.0

Table 2: Energy densities of metals and metal hydrides which evolve hydrogen in aqueous solution (100% material conversion).

however appear highly attractive for special-purpose applications including aerospace and/or military applications. In a direct comparison with alternative hydrogen storage materials and hydrogen generation reactions, silicon proves to be the best compromise between production costs and handling, not to mention the abundant, worldwide availability from sand. These relationships are illustrated in Figure 5 and Figure 6.²⁴ Whereas Figure 6 is based on element-specific and hence fixed data, Figure 5 includes aspects including silicon production costs. Silicon proves to be optimal with respect to handling and energy density relative to hydrogen storage and generation. Furthermore, the price of electricity in the mechanism $\text{SiO}_2 \rightarrow \text{Si} \rightarrow \text{H}_2 \rightarrow \text{Electricity}$ (given in €/kWh) decreases proportionately with the costs for the production of silicon. Our expectations for a solar-thermally produced carrier manufactured from conventional sand permit us to predict an unbeatable cost profile for silicon in the future.

As described in equation (4), silicon reacts with water under alkaline condition to form silicate and hydrogen. It is possible to recycle sodium hydroxide from the silicate (eq. 5) but the reaction is very slow.

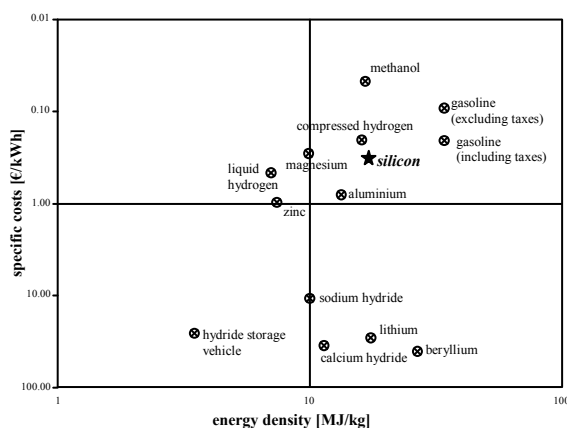


Figure 5: Energy carriers for hydrogen storage and generation (log-log scale, price September 2002).

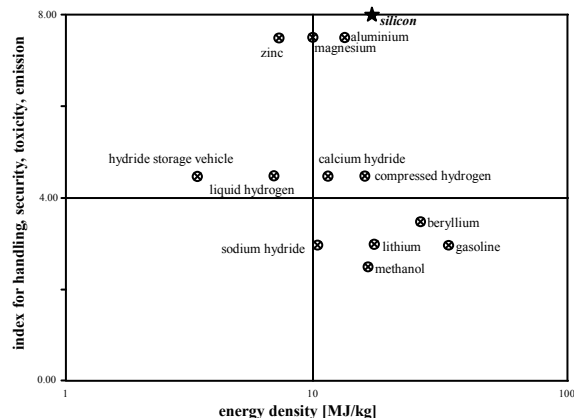
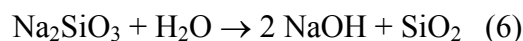


Figure 6: Energy carriers for the storage and generation of hydrogen (simple log scale).

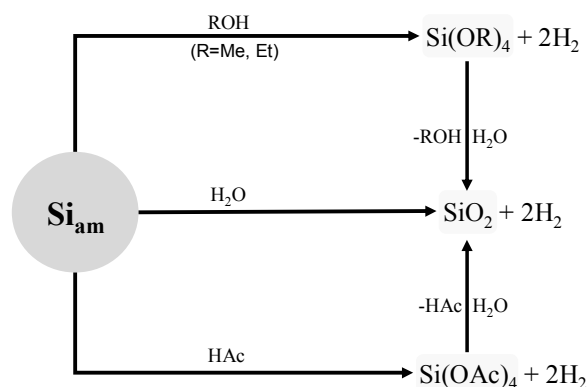
Calcium hydroxide is used as a catalyst which reacts to form calcium silicate.³⁰ The drawback of this mechanism is the high consumption of alkali, water and chalk. Furthermore the decomposition of calcium carbonate requires thermal energy and releases CO_2 . To overcome this problem, the reaction was optimised in accordance with equation (6) by generating the hydrogen in a reformer system under conditions of elevated temperature and pressure.³¹



Despite all these benefits a selective reaction of silicon with a single compound without the need for any further chemical components allowing the generation of hydrogen under moderate conditions is still desirable. And also possible! When highly reactive – but not spontaneously combustible – amorphous silicon produced via the halogen-silane-mechanism reacts directly with water at ambient temperatures ($T \sim 20 - 100^\circ \text{C}$), quantitative amounts of sand and hydrogen are formed.

Of even more interest, reactions of silicon with alcohols or carboxylic acids result in the formation of hydrogen and of commercially attractive silicon based functional chemicals suitable for industrial applications.³²

The different synthetic mechanisms for the formation of hydrogen from amorphous silicon are summarised in Scheme 1.



Scheme 1: Silicon as source of hydrogen.

If required these silicon compounds can be recycled by simple hydrolysis leading to sand and releasing the alcohol or acid initially used.

Silicon as an energy carrier – the general concept

The information provided in this paper describe a carbon/carbon dioxide-free mechanism to generate ammonia, the basic feed stock for fertilisers and possibly also a replacement for natural gas in combustion processes or as converter supply in fuel cells. Alternatively, ammonia can itself be used as a source of hydrogen. Furthermore, and this point appears to be the major potential of the concept due to the current situation where the macroeconomic financing of a comprehensive hydrogen-oriented infrastructure cannot be fully justified, it is technically possible to generate hydrogen directly from silicon at any location of choice avoiding the transport and storage difficulties encountered with conventional power stations and stationary/mobile fuel cells (Scheme 1). Of course, it is also possible to synthesise ammonia from hydrogen in a direct reaction with nitrogen in the Haber-Bosch process.

Thus, silicon successfully acts as a tailor-made intermediate linking decentrally operating renewable energy generation with equally decentrally organised hydrogen-based infrastructure at any location of choice.

Summary

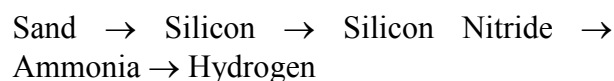
As carbon-based primary energy carriers become increasingly exhausted, it is obvious

that the existing reserves should be better used for the production of valuable products as opposed to carbon dioxide. The concept outlined here describes a practical solution to secure the future supply of ammonia and hydrogen via a “non-carbon” route for a range of applications.

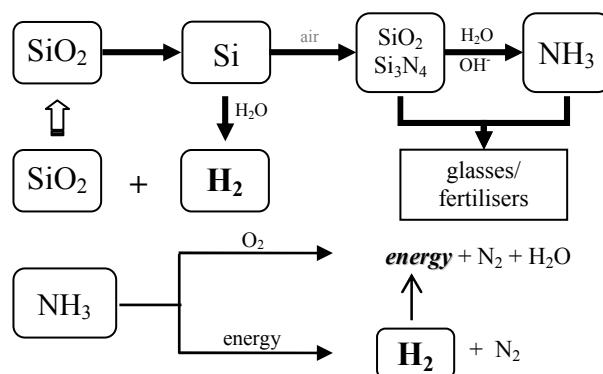
Furthermore, in addition to feed stock for the fertiliser industry, silicic acid (SiO_2) and silicon nitride (Si_3N_4), both ceramic materials of great economic value, can be manufactured via the reaction mechanism.

That means that, in addition to energy, the concept also provides useful silicon-based combustion products instead of carbon dioxide (Scheme 2).

Additionally, the hydrogen which is generated via the mechanism:



or directly from silicon and water or alcohols is “pure”. In strong contrast to oil and in particular hydrogen, the transport and storage of silicon are free from potential hazards and require a simple infrastructure similar to that needed for coal. Whereas the latter material is converted to carbon dioxide, sand is produced from the silicon which in turn can be used to prepare the silicon carrier material.

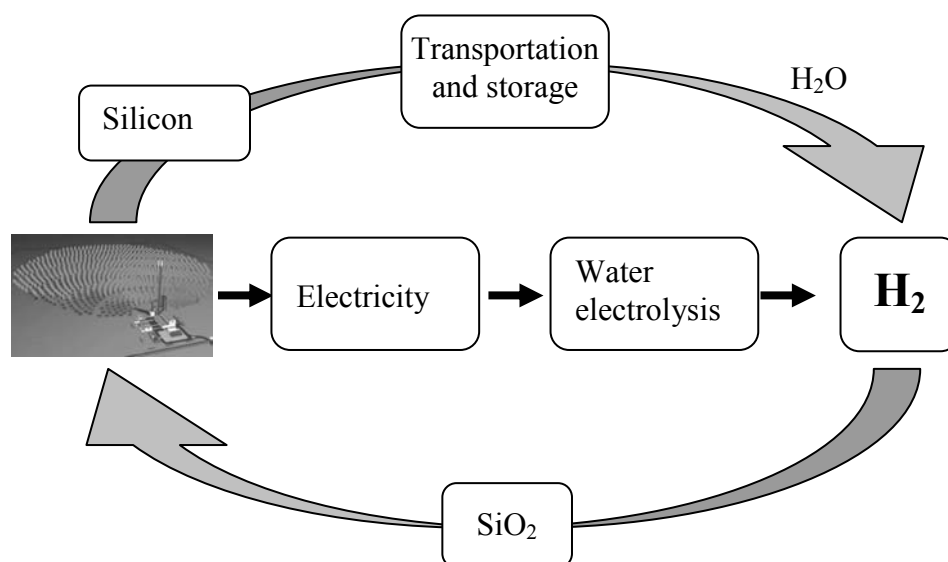


Scheme 2: Silicon as an energy carrier – the general process.

This concept of future energy supply based on hydrogen in effect represents the realisation of

Rifkin's vision described in the introduction:⁶ the 3-stage solar thermal generation of hydrogen from sand! Scheme 3 summarises Rifkin's idea of hydrogen production. The use of the element silicon represents an attractive solution to the problems resulting from efficiency losses during the conversion of thermal energy into electrical power as well as

the transport and storage difficulties associated with hydrogen. The scale-up of laboratory results to a technical and pilot scale along with further optimisation developments moving towards large-scale operations will demonstrate whether silicon can indeed solve all the forecasted energy problems in the future.



Scheme 3: J. Rifkin's idea for future energy supply. The utilisation of silicon as an energy carrier solves the problems associated with this.

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Many thanks to all my staff for their unabated efforts to solve the complexity of problems which continue to arise.

I thank my family and friends for their prolonged encouragement, to continue and to develop the concept even following experimental setbacks.

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Thanks to the companies Dow Corning Corporation (Midland, USA) and Wacker Chemie GmbH for specialist advice and the financial support to complete our work.

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- [2] International Hydrogen Energy Forum 2000 (HYFORUM 2000), 11.-15. September, München, Deutschland: *A statement of Green Peace*.^{a)}
- [3] Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit: *Erneuerbare Energien und Nachhaltige Entwicklung*, 3. Aufl., August 2000.
- [4] Estimations suggest that solar thermal usage of approximately 1% of the area of the Sahara would suffice in order to cover global energy requirements: H. Klaiß, F. Staiß (Hrsgb.): *Solarthermische Kraftwerke für den Mittelmeerraum*, Band 1: Gesamtübersicht, Marktpotential und CO₂-Reduktion, Springer-Verlag, Berlin 1992.

- [5] J. Gretz: *Wasserstoff als Energieträger eines sauberen Energiebereitstellungs-systems mit direkter und indirekter Sonnenenergie, Konzept eines Pilotprojektes*. In: Dechema-Monographien, Band 106. Weinheim: VCH Verlagsgesellschaft, 1986. V.U. Hoffmann: *Wasserstoff – Energie mit Zukunft*. 2. Auflage. Stuttgart: Teubner Verlag, 1994.
- [6] In a presentation at the “Medienforum Deutscher Wasserstofftag“, 1. Oktober 2003, München: *The hydrogen revolution plea for a hydrogen community* Jeremy Rifkin (Washington DC), best-selling author and environmental activist, suggested the following solution: renewable energies should be transformed into electrical current which is used for electrolysis of water. The resulting hydrogen in gaseous or condensed form is transported to a location of high energy requirement where it is stored and used to generate energy as required. This leads to the following sequence: Renewable energy → electricity → electrolysis of water → hydrogen. Based upon the problems associated with this in principle correct sequence, the author attempts to describe the current situation as a background to this idea aimed at overcoming the inherent difficulties.
- [7] A.F. Hollemann, N. Wiberg: *Lehrbuch der Anorganischen Chemie*, 101. Aufl., Berlin/New York: de Gruyter Verlag, 1995.
- [8] *CRC Handbook of Chemistry and Physics*, 73rd Ed, D.R. Lide, editor, Boca Raton/Ann Arbor /London/Tokyo: CRC Press, 1992-1993.
- [9] This value contains various forms of biomass including plants (e.g. combustion residue from rice plants which are very common in Asia) or diatoms (in sea water), geological products etc. The element silicon is, with the exception of oxygen, the second most abundant chemical element with a presence in the earth as great as all the other elements together.⁷
- [10] A. Schei, J.K. Tuset, H. Tveit: *Production of high silicon alloys*, Trondheim, Tapir Verlag, 1998.
- [11] Based upon these cost factors, the current price of silicon is approx. USD 1,200 per tonne; for ferrosilicon, e.g. a mixture comprising approx. 75% Fe, this price is halved to about USD 600.
- [12] N. Auner, S. Holl: *Silicium als Energieträger – Fakten und Perspektiven*, Praxis der Naturwissenschaften, Chemie in der Schule 52(8), 2003, 2-7; N. Auner, ECOS 2003, June 30 – July 2, 2003, Copenhagen (Denmark), Abt. Energy Management by Energy Storage, Abstracts p. 601 – 608: *Silicon als Energy Carrier – Facts and Perspectives*.
- [13] It appears particularly attractive to carry out solarthermic reactions in regions of large sand deposits and intensive sun light (e.g. in the desert). Using specially erected large-scale reflectors, solar energy can be used to generate focussed high temperatures (up to 2,500° C) and electrical current with an efficiency of 30 – 40%.¹⁴ In the process described in this article, sand is converted to silicon tetrahalogenides at temperatures between 20 and 1,000° C. The exact temperature depends upon the selection of halogen compound. These tetrahalogenides are thermally decomposed to elementary silicon at approx. 1,000° C. The original halogen compound is formed once again during this process, representing a recycling rather than a consumption mechanism. This renders this silicon manufacturing process particularly efficient and attractive.
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- [16] Thanks to Paul Scherrer Institut, Villigen (Switzerland) for providing the electrochemical and thermodynamic data (including experimental determinations).

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- [21] N. Auner, J. Elsner: *Gasphasen-Erzeugung und Reaktionen hochreaktiver Silicium-Fragmente*, J.W.G.-Universität Frankfurt, Dissertation, 2004.
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- [23] E.R. Weaver: *The Generation of Hydrogen by the Reaction between Ferrosilicon and a Solution of Sodium Hydroxide*. The Journal of Industrial and Engineering Chemistry, 12, 1920, 232- 40.
- [24] D. Herbst: *Untersuchung der Eignung eines neuartigen Verfahrens zur Erzeugung von Wasserstoff mit Hilfe von Silicium für den Einsatz in Kraftfahrzeugen*, Institut für Maschinen-Konstruktionslehre und Kraftfahrzeugbau, Universität Karlsruhe (TH), Dissertation 2003.
- [25] Lithium hydride has often been used to generate hydrogen on a technical scale as this exhibits the greatest energy density of all the alkali metal hydrides. Large-scale deployment has been hindered by the high flammability, scarcity and high costs. Sodium hydride is significantly less expensive but has a far greater reactivity than the lithium compound which necessitates increased safety precautions during storage and renders the controlled release of hydrogen more difficult. Use of calcium hydride to produce hydrogen is known from the “hydrolith process” [E.D. Arbery: *Wasserstoff für militärische Zwecke*. Chemiker-Zeitung 40, 1916, 928]. The benefit of these alkaline earth hydrides is due to their relative high stability to reaction which permits hazard-free handling in air and also a controlled release of hydrogen.
- [26] The element beryllium has the highest energy density of all metals. By passivation of the surface with an oxide layer, it can be stabilised almost indefinitely and made safe for transport. Hydrogen is released by reaction with dilute sodium hydroxide. However, beryllium is extremely expensive due to the fact that the composition in the earth’s crust is a mere 4 – 6 ppm (price approx. USD 620 per kg). The largest K.O. factor however is the toxicity as the water-soluble salts are absorbed by the human body [W. Schreiter: *Seltene Metalle* (Band 1). 2. Aufl., Leipzig: Deutscher Verlag für Grundstoffindustrie 1963].
- [27] Aluminium is attractive as an energy carrier due to its ready availability and high energy density. The technical production capacity is also high. However, the surface of aluminium is passivated by an oxide layer which makes the decomposition by water possible only in the presence of amalgam. In the absence of amalgam, bases cause the decomposition of Al via: $\text{Al} + \text{NaOH} + 3 \text{H}_2\text{O} \rightarrow \text{Na}[\text{Al}(\text{OH})_4] + 1\frac{1}{2}\text{H}_2$. The spent sodium hydroxide can be regenerated: $\text{Na}[\text{Al}(\text{OH})_4] \rightarrow \text{Al}(\text{OH})_3 + \text{NaOH}$. However, this leads to an excessive consumption of water and to a high-weight final product. Aluminium and amalgam are not suited for the generation of hydrogen on a technical scale because of mercury vapour

- which is carried by the hydrogen gas and which requires great efforts to be removed.
- [28] The arguments against zinc to generate hydrogen resemble those for aluminium. Zinc is inert towards pH neutral water due to the passivating hydroxide surface layer. In contrast, zinc is decomposed by bases to give hydrogen: $\text{Zn} + 2 \text{NaOH} + 2 \text{H}_2\text{O} \rightarrow \text{Na}_2[\text{Zn}(\text{OH})_4] + \text{H}_2$. The tetrahydro zincate produced can be used to regenerate sodium hydroxide; however, this is an expensive process. Also, the significantly lower energy density does not favour its use in the generation of hydrogen.
- [29] Alkali boranates and alanates can cause large volumes of hydrogen to be released. Only the sodium salts NaBH_4 and NaAlH_4 are of interest because of costs. The reaction of sodium borohydride with water leads to sodium metaborate, NaBO_2 . The US company Millennium Cell is currently developing mobile hydrogen generators on the basis of sodium boranate [*The British Admiralty Hydrogen Gas Plant: Engineering* 107, 1919, 102]. Sodium boranate has the advantage that it reacts with water only in the presence of noble metal catalysts [S.C. Amendola, S.L. Sharp-Goldman, M. Saleem Janjua, M.T. Kelly, P.J. Pettilo, M. Binder: *An ultrasafe hydrogen generator: aqueous, alkaline borohydride solutions and Ru catalysts*. *J. Power Sources* 85, 2000, 186 – 189] and can thus be stored and transported as aqueous solutions [S.C. Amendola, S.L. Sharp-Goldman, M. Saleem Janjua, N.C. Spencer, M.T. Kelly, P.J. Pettilo, M. Binder: *A safe, portable hydrogen gas generator using aqueous borohydride solution and Ru catalyst*. *Int. J. Hydrogen Energy* 25, 2000, 969 – 975]. In contrast sodium alanate requires high levels of water consumption since hydrate-rich sodium aluminium hydroxide $\text{Na}[\text{Al}(\text{OH})_4]$ of high specific weight is formed. The recycling of the conversion products means that unnecessary large volumes of substance need to be returned to the supplier. Both compounds, NaBH_4 and NaAlH_4 are water soluble which means that special and expensive safety precautions are necessary during transport and storage.
- [30] A. Sander: *Die Darstellung von Ballongasen*. *Zeitschrift für Angewandte Chemie* 24, 1911, 195-200.
- [31] D. Herbst, *Verfahren und Vorrichtung zur Herstellung von Wasserstoff*. *Deutsche Offenlegungsschrift* 1 99 54 513, 1998. D. Herbst: *Verfahren und Vorrichtung zur Herstellung von Wasserstoff*. *Deutsche Offenlegungsschrift* 1 01 55 171. D. Herbst: *Wasserstoffspeicherung in Silizium – Alternative als Kraftstoff für Brennstoffzellen*. *ATZ, Automobiltechnische Zeitschrift* 102 (7/8), 2000, 622-627. D. Herbst: *Silizium für Sekundärenergie*. *BWK Brennstoff Wärme Kraft* 52 (7/8), 2000; 52-55.
- [32] The generation of hydrogen by conversion of silicon with biologically prepared methanol appears highly attractive since the C1 component formed via photosynthesis does not react to produce CO_2 as in the conventional reformer process ($\text{CH}_3\text{OH} + 0.2 \text{H}_2\text{O} + 0.4 \text{O}_2 \rightarrow 2.2 \text{H}_2 + \text{CO}_2$) which is irreversibly released to the detriment of the environment. In this case, it can be recycled and returned to the system by $\text{Si}(\text{OCH}_3)_4$ hydrolysis [$\text{Si}(\text{OCH}_3)_4 + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{CH}_3\text{OH}$].

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