Hydrogen Recharge Dynamics and Vessel Design for Porous Silicon Storage Media

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ABSTRACT

Results are presented for the design of a complete hydrogen storage system capable of energy density greater than 5.9 % by weight. This system uses moderate pressures and temperatures, and recharges in under 7 hours. Recharge in 3.5 minutes is achievable, albeit with a storage density of 4.9% w/w owing to the higher pressures and thicker vessel walls required. Storage media costs are estimated at 7.72 USD/kWh, a factor of 20 lower than Li-ion batteries. These metrics show the promise of using catalytically-modified porous silicon as a useful hydrogen storage media.

Keywords: hydrogen, storage, porous, silicon, catalyst, spillover.

1 INTRODUCTION

Spillover of hydrogen atoms in solid state media allows high energy storage density. The use of porous materials allows heat exchange via hydrogen gas, as well as facile diffusion therethrough. Storage media transparent to infrared light permits dual-mode control over temperature internal to the matrix. Catalytically-modified porous silicon has all of these attributes, and with binding energy lower than for carbon, making porous silicon an interesting candidate for solid state hydrogen storage.

Porous silicon has been demonstrated to store hydrogen at up to 6.6 % w/w [Lysenko], with a theoretical limit estimated at 7.1% [Schubert 2006]. Silicon is transparent to infrared light at wavelengths longer than about 660 nm [Sze]. A novel method for introducing a spillover catalyst onto an actives support has been recently patented for the case of palladium on porous silicon [Schubert 2013]. In this work the thermodynamics of hydrogen recharge are examined theoretically to determine the pressure, temperature, and recharge duration for catalytically-modified porous silicon. Computations are extended to the vessel for enclosing the storage media, to determine the mass and arrive at an estimate of the system-level storage density.

2 METHODS

Ab initio calculations assuming a Knudsen diffusion model are used to determine the recharge duration as a function of temperature and pressure. Within this trade space, two use case scenarios are studied, such that the temperatures and pressures required dictate the choice of vessel materials and the thickness of the walls required. Safety margins are applied to these theoretical values to arrive at practical vessel masses for each scenario. Adding generic masses for control electronics and brackets/fittings the system-level hydrogen storage density can then be computed. For both scenarios a 5 kilogram charge of hydrogen is assumed, allowing comparison with competing methods of hydrogen storage, and validation against the 2017 goals established by the US Department of Energy [US DOE].

2.1 Spillover Recharge

Two key papers describe the energy relationships for the spillover effect [Xiao, Leuking]. Porous silicon is initially synthesized in aqueous solution via electrochemical etching in hydrofluoric acid at 70 mA/cm^2, leaving hydrogen-terminated silicon bonds in a matrix of about 75 percent open space and pores of lesser than 5 nm in diameter. Thermal discharge is used to measure the hydrogen storage percentage, however, complete discharge of the as-synthesized material occurs at temperatures sufficiently high that bond reforming occurs between adjacent vacant bonds on the porous silicon matrix. Partial discharge of about 0.03 of the total hydrogen initial charge is accomplished by heating to a temperature slightly higher than the temperature at which spontaneous discharge begins to occur. The matrix is then cooled and returned to an aqueous solution where catalytic atoms are deposited to the bond sites recently vacated of their hydrogen termination. These sites are believed to occur preferentially at triply-terminated silicon bonds at the verges of the internal fractal topology of the porous matrix. Palladium is the catalyst of choice due to its known affinity for silicon. This catalyst atom now forms a site where gaseous diatomic hydrogen molecules can associate and dissociate [Rahimi]. The presence of this catalyst, in intimate contact with the storage media-cum-support, now lowers the energy barrier to hydrogen desorption, allowing it to occur at lower temperatures [Schubert & Wilks]. Bond reformation is greatly reduced thereby. During recharge the dissociated hydrogen atoms at the catalyst sites can bond-hop to adjacent vacant bonds, which can in turn bond-hop to their neighbors. This is an explanation of the spillover effect, and can be treated using mathematical methods developed on similar catalyst/support systems.

2.2 Heat and Mass Transfer

Recharging hydrogen onto porous silicon is nearly net zero energy, neither endothermic or exothermic [Schubert & Wilks]. Recharge durations are affected by temperature and pressure through the activity and potential energy. Heating the storage matrix to the desired temperature is assumed to be performed with infra-red (IR) heat lamps, mounted flush against the interior wall of the vessel enclosing the hydrogen storage media. IR light of about 660 nm passes through bulk silicon, and is absorbed by single-terminated Si-H bonds. Such IR radiation can thus be used to set the temperature of the media to achieve the desired recharge dynamics.

Heat transfer into and out of the porous silicon matrix is assumed to be much faster than the spillover effect. The reasons for this assumption are: (1) IR heating affects the bulk, and not just the surface of the matrix; (2) IR light passing entirely thorough the porous silicon matrix will simply warm the interior walls on the opposing side of the vessel; and (3) hydrogen has both a very high diffusivity and high thermal heat capacity, so it can carry heat throughout the porous matrix bulk at rates faster than the spillover kinetics.

2.3 System Design

The ab initio calculations yield a family of curves for recharge time as a function of temperature and pressure. Temperature is used to identify materials which can be used and pressure determines the strength requirement of the vessel walls, dictating the minimum shell thickness. The optimal geometry for the vessel which takes into account both strength and ease of manufacture is a cylindrical shape. A variety of options exist for design of the vessel ends, but this analysis will explore the hemispherical geometric configuration.

In the scenarios which follow, ASME standards apply as internal design pressure exceed 14.7 pounds per square inch (PSI), and the diameter of the cylindrical vessel is greater than 6 inches. This imposes a required safety margin resulting in a greater thickness measurement and thus a heavier vessel.

The equation governing the required thickness due to internal pressure in the circumferential direction for thin cylindrical shells is given by:

$$t = \frac{P \cdot R}{S \cdot E - 0.6 \cdot P} \quad t < 0.5R \qquad (1)$$

Similarly, the equation used to determine thickness required in the longitudinal direction is in the form:

$$t = \frac{P \cdot R}{2 \cdot S \cdot E + 0.4 \cdot P} \quad t < 0.5R \qquad (2)$$

In both equations, P is the design pressure, R is the internal radius, S is the allowable material stress, and E is the weld joint efficiency factor [Farr]. The allowable stress, S, is based on the tensile strength of the material of construction adjusted for the safety factor of 4 as governed by ASME Section VIII Pressure Vessels, Division 1 [Megyesy].

Since the thickness required in the circumferential direction is greater (by a factor of 2) than that which is required in the longitudinal direction, Eqn (1) will be used to establish the thickness of the vessel as it overrides Eqn (2) and represents the worst case condition and highest level of stress to which the vessel should be designed.

The mass of the vessel is determined using the calcuated thickness and material density, along with volume equations in which the radius value is selected strategically so that a practical geometry of the vessel is obtained.

To the mass of the vessel are added the following masses to make a complete system calculation: control electronics: 0.25 kg; valve, connectors, fittings: 0.35 kg; relieve ports and brackets: 0.25 kg. These assumptions are fixed for each case study of a 5 kg charge of hydrogen.

3 RECHARGE

The movement of silicon atoms into the matrix is modeled using Knudsen diffusion, dominated by molecule-wall collisions [Xiao]. The diffusion coefficient for hydrogen atoms moving on the surface of silicon is given by:

$$D = \frac{1}{z} v_e \alpha^2 \exp(-\frac{E_a}{kT}) \qquad (3)$$

where v_e is the effective vibrational frequency of the molecule and is estimated at 1E13 Hz [Schubert & Wilks], z is the number of adjacent sites for bond-hopping ("coordination number", taken to be 4), and α is the nearest-neighbor distance in the silicon lattice. The activation energy E_a is 71.4 kcal/mol for the Si-H bond [Weast].

According to Fick's first law of diffusion, the net diffusive flux of one species in a given direction is related to the gradient of the concentration of this species by a phenomenological relation of the form:

$$J_x = -D \frac{\partial n}{\partial x} \qquad (4)$$

The concentration gradient is determined by the applied pressure P, through differentiation of the ideal gas law:

$$\frac{\partial n}{\partial x} = \frac{P N_A}{RT\alpha} \qquad (5)$$

Where N_A is Avogadro's number. Inserting eqs. (3) and (5) into (4), and calculating across a matrix of pressure and temperature provides the recharge rate.

Pore sizes in silicon are measured to be about 3.5 nm in diameter. Pore depth is approximately 150 microns. Pores are modeled as empty cylinders perpendicular to the original silicon surface. Recharge times are computed as the ratio of the number of interior vacant bonds to be filled divided by the product of the diffusion flux and the area of the open end of the pore.

4 VESSEL DESIGN

The family of curves derived herein indicate a tradeoff between fast recharge and high energy density cannot be realized simultaneously with a porous silicon storage media. Therefore, the results are bifurcated into two alternate embodiments, or use-case scenarios. The first is for home or personal use where a charge time of 7 hours is considered no inconvenience, and is called the "slow home" scenario. The second is for fleet vehicles needing rapid recharge in a format which may be less sensitive to cost or mass, called the "fast fleet" scenario.

In both cases, the overarching goal is to obtain the lowest mass and most economical design attainable for the entire storage system including vessel, valves and fittings. Figures 1 and 2 for "Slow Home" and "Fast Fleet," respectively, can be analyzed to identify optimal operating parameters for each application. For a given fill time, there is a trade-off between pressure and temperature variables. For example, selecting a lower temperature results in a higher pressure required to achieve the same fill rate, and vice versa. The relationship between pressure and temperature needs to be considered as the analysis of materials of construction is performed because this drives weight and cost of the system. Various materials were evaluated including polymers, aircraft aluminum, carbon steel, and stainless steel.

4.1 Design Considerations

Materials of Construction:
Polymers, which represent the lightest weight family of materials, was eliminated due to the anecdotally-reported inability to contain pressures greater than atmospheric or 14.7 PSI. The next lightest material considered was 6000 Series Aluminum and is suitable only for temperatures up to 204 C. Carbon steel was not considered an option due to concerns over hydrogen embrittlement. Low-carbon stainless steel is a versatile material and can be used for both "slow home" and "fast fleet" applications, but is more costly than either aircraft aluminum or carbon steel.

Vessel Volume and Mass Limits Calculated for 5 Kg H_2 Storage System
Using the DOE Targets for Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles, the System Gravimetric Capacity of 0.055 kg H_2/kg system and the System Volumetric Capacity of 0.040 kgH_2/L system equate to a

maximum system mass of 90.5 kg, and maximum system volume of 125 L. Design calculations performed for the porous silicon system indicate a required vessel capacity of 130 L to effectively contain the storage media, close to, but not yet within, the 2017 DOE targets for light-duty vehicles. If the theroetically possible 7.1% w/w storage is possible, then we can meet the system volumteric capacity target.

4.2 System Level Metrics

"Slow Home" Scenario
The Slow Home scenario has the added advantage of a wider range of fill times allowed and thus offers several possible pressure and temperature operating parameters. The lightest weight and most economical design is achieved by maximizing fill time while minimizing pressure and temperature requirements. The optimal point on the graph occurs at the fill time of 400 minutes, slightly shorter in duration than a typical human sleep cycle. The corresponding values for temperature and pressure are 150 C and 2.4 bar Taking into account process variability of the control variables temperature and pressure, adjustments of + 30 C for temperature and +15% for pressure are made. This establishes upper limits for each which are indicated in Table 1. Converting to USCS units, the resulting design parameters are 360 F and 71 PSI. These findings are significant because the data suggest that aluminum is an acceptable material of construction.
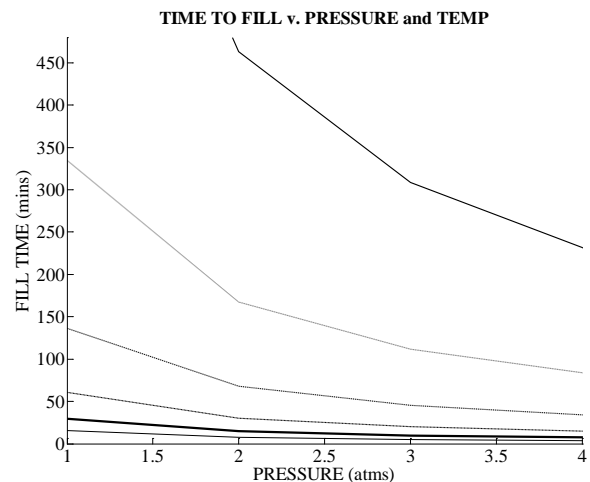

TIME TO FILL v. PRESSURE and TEMP

Figure 1: Fill time as function of pressure and temperature for "Slow Home" recharge scenario. Contour lines increment by 25 C, moving downward, starting at 150.

	Pressure	Temperature
Value from Graph	2.4 bar	150 C
Control Upper Limit	2.8 bar	180 C
Conversion to USCS	41 PSI	360 F

Table 1:Calculation of Design Parameters for "Slow Home"

Equation (1) is used to calculate the vessel thickness required for the operating pressure specified. The ultimate tensile strength for the recommended material Aluminum 6061-T6 is 45 ksi (thousand PSI) [ASM]. Applying the ASME Section VIII, Division 1 safety factor of 4, the maximum allowable stress for the material is 11.25 ksi. The vessel volume is fixed, and radius minimization is sought in order to minimize the thickness, but the corresponding length must be considered to ensure the geometry is suitable for the application. In practice, typical joint efficiency factors range between of 0.7 and 1. For the purpose of this analysis the mean value of 0.85 for E is employed. With an internal radius of 7.0 inches one obtains a vessel length of just over 56 inches with thickness of 0.052 in. Using 0.0975 lb/ in^3 as the value for density [ASM] and the aforementioned physical properties, the vessel mass is determined to be 7.3 lbs. The estimated total system mass including H_2, the silicon media, vessel, valves and fittings is 188 lbs. or 85 kg. The calculated system gravimetric capacity is 5.9 % and the volumetric capacity obtained for 5 kg H_2 contained within a 130L system is 3.8 %.

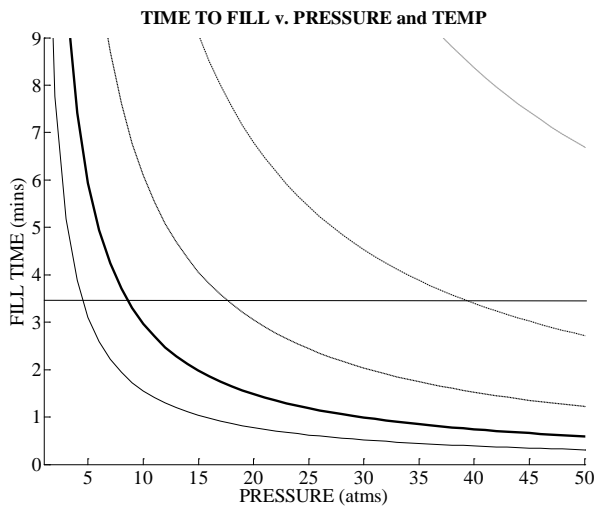### "Fast Fleet" Scenario

TIME TO FILL v. PRESSURE and TEMP

Figure 2. Fill time as function of pressure and temperature for "Fast Fleet" recharge scenario. Contour lines increment from 125 C by 25 C – bolded line (second lowest) is 250 C. DOE target of 3.5 minutes indicated.

The DOE target for fill time has been set as 3.5 minutes for the Fast Fleet" application in the transport industry for light-duty vehicles. This target creates a constraint on the hydrogen storage system, as higher values of pressure and temperature are required. Aluminum alloys are not an option for this application, so 316L (low-carbon) stainless steel is considered. Temperature is less of a concern with stainless steel, and is set as high as practical while remaining below 275 C, the temperature at which bond reforming begins to occur in porous silicon. At this temperature the recharge pressure is 8.5 bar. Process variability must be taken into account for design considerations, thus upper limits are calculated and indicated in Table 2. Temperature control will be important, and calls for an underdamped control system to avoid thermal overages.

	Pressure	Temperature
Value from Graph	8.5 bar	250 C
Control Upper Limit	9.8 bar	275 C
Conversion to USCS	144 PSI	540 F

Table 2: Calculation of Design Parameters for "Fast Fleet"

Equation (1) is used to calculate the vessel thickness required for the maximum operating pressure specified. The ultimate tensile yield strength for the recommended material 316L SS at 316 deg C (600 F) is 78 ksi [AK Steel]. Applying the ASME Section VIII, Division 1 safety factor of 4, the maximum allowable stress for the material is 19.5 ksi. As in the previous scenario, the vessel volume is fixed, and in order to minimize thickness and weight, a minimal value for vessel radius is chosen which obtains a suitable length for the application. Weld joint efficiency factor is set at 0.85. Selecting the measurement 6.5 inches for the radius obtains an overall vessel length of 64 inches and shell thickness of 0.10 in. The material density is 0.29 lb/ in^3 for 316L SS [AK Steel], and a cylindrical vessel with these dimensions and properties has a mass of 43 lbs. The estimated total system mass including H_2, silicon media, vessel, valves and fittings is 223 lbs or 102 kg. This results in a system gravimetric capacity of 4.9 %. The calculated system volumetric capacity obtained for 5 kg H_2 contained within a 130L system is 3.8 %.

5   DISCUSSION

In both the "slow home" and "fast fleet"scenarios, the equation used to calculate thickness required for the entire storage vessel including the ends was based on a cylindrical shell with hemispherical end caps. In reality, the thickness of spherical ends is determined through utilization of an alternative equation which yields a value essentially one-half that of the cylindrical shell. Therefore, the weight value which is used in this analysis is higher than would be expected in the real-life application. The weight of the storage media contained within the vessel and its impact on the effective internal pressure, due to gravity, was considered and found to be negligible (< 0.5%). The 5.9% gravimetric capacity obtained for the "slow home" case exceeds the DOE target of 5.5 %. Decreasing the fill time to 3.5 minutes and speeding up the recharge rate ("fast fleet") results in a gravimetric capacity value of 4.9% which does not quite meet the target. The volumteric capacity in both cases was determined to be 3.8% compared to the DOE target of 4.0%. It is possible for the volumetric capacity to reach this target if the theoretical value of 7.1% w/w is achieved.

	DOE Target	Slow Home	Fast Fleet
Fill Time	3.5 min	7 hours	3.5 min
Media Cost	12	7.72	7.72
Grav. Cap..	5.5%	5.9%	4.9%
Volum. Cap.	4.0 %	3.8%	3.8%

Table 3: Data Comparison to DOE Targets

6   CONCLUSION

Hydrogen storage using catalytically-modified porous silicon has the potential to readily meet two of the key 2017 DOE metrics for on-board hydrogen storage systems in light-duty vehicles. Of the other two metrics one or the other can be achieved for a given hardware configuration and recharging scenario.   That this relatively unknown method for solid state hydrogen storage can meet three of the four criteria is an indication of the potential for this novel system.

7   ACKNOWLEDGEMENTS

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