

# Rapid Discharge of Solid-State Hydrogen Storage Using Porous Silicon and Metal Foam

Loralee P. Potter, Peter J. Schubert

**Abstract**—Solid-state hydrogen storage using catalytically-modified porous silicon can be rapidly charged at moderate pressures (8 bar) without exothermic runaway. Discharge requires temperatures of approximately 110°C, so for larger storage vessels a means is required for thermal energy to penetrate bulk storage media. This can be realized with low-density metal foams, such as Celmet™. This study explores several material and dimensional choices of the metal foam to produce rapid heating of bulk silicon particulates. Experiments run under vacuum and in a pressurized hydrogen environment bracket conditions of empty and full hydrogen storage vessels, respectively. Curve-fitting of the heating profiles at various distances from an external heat source is used to derive both a time delay and a characteristic time constant. System performance metrics of a hydrogen storage subsystem are derived from the experimental results. A techno-economic analysis of the silicon and metal foam provides comparison with other methods of storing hydrogen for mobile and portable applications.

**Keywords**—Conduction, convection, kinetics, fuel cell.

## I. INTRODUCTION

**H**YDROGEN storage and transportation are crucial objectives in reaching a feasible hydrogen energy economy. The storage capacity for solid systems can be higher than gas- and liquid-based alternatives but solid-state technologies for hydrogen remain inefficient, or unable to be recharged. Material-based storage systems are widely regarded as safer alternatives to compressed gas and cryogenic hydrogen storage due to their intrinsic stability, and are at the forefront of research objectives. Metal hydrides are problematic for vehicle use due to expansion that places undue stress on the system, slow kinetics, and highly exothermic conditions created during system charging. Porous silicon provides a lightweight solid storage media which does not suffer the high heat and expansion created during recharge cycles by metal hydride systems [1].

Silicon has long been investigated as a hydrogen storage material, but moderate hydrogen sorption and high activation energy in hydrogen release must first be overcome. Hydrogen storage on silicon directly corresponds to available silicon surface area [2]. It's also been proposed that with a suitable catalyst, the activation energy of hydrogen released can be lowered to the point of a reversible system [3]. Palladium hydride stores 0.56% hydrogen by weight, but even more useful is that this occurs at ambient conditions with a pressure of 0.02 bar and temperature of 298K [4]. A palladium catalyst that is dispersed on the surface of porous silicon provides area for

surface diffusion of hydrogen atoms between palladium clusters that transfer onto and off of the catalyst particles via spillover [5]. This system has the potential to decrease the hydrogen bonding energy to be viable at the temperature of a proton-exchange membrane fuel cell. Catalytically-modified porous silicon, ideally silicon nanoparticles, provides a promising automotive hydrogen storage solution.

A three-dimensional solid-state hydrogen storage system requires a robust framework to maintain system integrity while allowing for rapid heating of the entire system to efficiently release stored hydrogen. Celmet™ metal foam is to be used as a structural support for the granular (particulate) silicon to prevent settling and compaction in a fuel cell vehicle (FCV), or other vibration-prone uses. Celmet is a low-density metal material having a three-dimensional spongelike structure achieving up to 98% porosity and able to maintain up to 90% porosity under half thickness compression [6]. The addition of a heat conducting metal framework is expected to increase thermal conductivity so that heat energy can reach the interior of a hydrogen storage vessel quickly facilitating rapid hydrogen discharge. Rapid response is important for most FCV applications, especially passenger vehicles which sometimes demand rapid acceleration. Including Celmet foam in a solid-state hydrogen storage vessel is expected to increase performance, both because of easier hydrogen diffusion, and because of faster heat-up.

This work investigates the thermokinetic properties of a novel design for silicon-based hydrogen storage supported by metal foam. In particular the choice of metal (Al, Cu, Ni) and metal foam pore morphology are evaluated in gaseous conditions bracketing the extremes of a completely full and a nearly-empty hydrogen storage subsystem. Silicon particle size is also varied, as this is expected to affect the balance between solid conduction of heat and gaseous convection of heat from the source through a composite porous silicon-metal foam matrix.

## II. MATERIALS AND METHODS

### A. Celmet™ Properties

Celmet™ is a lightweight sponge-like metal foam available from Innovation Core SEI [6]. Foams of high porosity are available in a variety of pore sizes, metals, and film thicknesses. Table I shows the parameters of three Celmet films used in the present study.

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TABLE I  
 CELMET™ PROPERTIES

Product identifier	Number of cells (/inch)	Cell size (mm)	Pore size (mm)	Thickness (mm)
Ni 450	55	0.45	0.23	1.2
Ni 510	50	0.51	0.26	1.2
Ni 850	30	0.85	0.43	2.4

Celmet consists of open-cell pores formed inside of dodecahedron shaped metal cells. Table I indicates properties of nickel Celmet varieties tested. As the number increases, the material is 'stretched'. Pore size and cell size increase while number of cells per inch is reduced. These properties follow the same pattern for Celmet sheets of metal composition other than Ni, such as Cu and Al.

### B. Fixture Design and Operation

A sealable low-carbon stainless steel testing apparatus was fabricated for this research. The material was chosen for its versatility with high pressures, temperatures, and resistance to hydrogen embrittlement. Main components included a 1000 cm<sup>3</sup> inner chamber, lid sealed with a Viton™ flange and 16 bolts. A passthrough admits 10 type K thermocouples to be embedded within stacks of metal foam in which their interstices are filled with silicon particles. Hydrogen or vacuum can be exchanged through a welded Swagelok® fitting. Heater element tape was affixed intimately to the bottom surface of the test fixture. Fig. 1 shows the fixture with the lid open.



Fig. 1 Test apparatus with Celmet and silicon powder just before sealing. From left to right: lid, Viton™ gasket surrounding thermocouples, flange, 1000 cm<sup>3</sup> chamber with flange

Prior to each test the sealed samples and fixture interior were exposed to mechanical vacuum for 15 minutes. For testing in a hydrogen environment, the fixture was pressurized with hydrogen gas to a pressure of 8.5 bar. Testing began at an ambient temperature of 20°C. At the start of each thermokinetic experiment, power was delivered to the heater element through a PID controller and a solid-state relay. In each case, the controller was set to reach 135°C. Each run was 1500 seconds in duration. Data was collected from the data acquisition system from Measurement Computing, model USB-2416.

### C. Silicon Infiltration & TC Placement

Thermocouple (TC) 0 was routed along an interior edge of the cubic test fixture, then along the same bottom face as had

the heater elements affixed. The junction rested on this surface as a reference, and was placed 1.5 cm from the center of the fixture. Celmet sheet 1 was placed on top of TC0. Celmet sheets were individually infiltrated with 99+% silicon metal powder using a sifting technique. Particles were placed on a razor-edged metal blade at a 15° angle on one edge of an extraneous Celmet sheet. A second razor blade at a 145° angle was dragged across the extraneous Celmet sheet with moderate pressure to completely cover the sheet in a layer of silicon particles. This loaded sheet was then held 15 cm over Celmet sheet 1 which had been placed in the bottom of the thermokinetic fixture. A small Teflon spatula was used to firmly tap the side of the lifted sheet, allowing the loaded particles to sift through the extraneous sheet. This method precluded clumping of the silicon powder. Sifting was continued until the bottom sheet was completely covered in sifted silicon particles. Celmet 1 was gently tapped with the spatula, and the sifting/infiltration process was repeated until particle settling ceased in the bottom sheet and it was deemed to have reached maximum particle infiltration. TC placement and Celmet infiltration processes were repeated in successive layers until all sheets and TCs had been placed. To maintain approximate radial symmetry, sequential TC wires were placed in different interior corners. An 8 cm stainless steel plate was placed on top of the final stack to maintain a compressed system during testing. Ten to 13 sheets of Celmet were used to create each stack for thermokinetic testing. For Ni 850, 10 thermocouples were layered between each of 10 total Celmet sheets. TC9, furthest from the heat source, rested between sheets 9 and 10. Thinner varieties of Celmet, specifically Ni 510, Cu 550, and Al 550 required 13 total sheets to achieve similar stack heights to Ni 850. For stacks composed of 13 sheets, TC numbers 1-7 were layered between each sheet, while TC 8 was placed between sheets 8 and 9, and TC 9 was placed between sheets 12-13.

### D. Cross-Sectioning Technique

Two-layer stacks of Celmet were used to study how well silicon particles filled the dodecahedral voids in the metal foam. The edges of the dual-stack were affixed with masking tape onto a stiff plastic tray. The stack was infiltrated using the method described in Section II.C. Low viscosity Stycast 1266 A/B epoxy resin was mixed per the directions. The infiltrated stack was heated to 60°C to reduce the viscosity of the resin and thus aid in the filling of voids, then the epoxy was applied. After curing for 24 hours, the plastic tray was cut away and a wet saw was used to cut 10 mm cross-sections of the Celmet stacks for edge-on inspection.

### E. Method of Thermokinetic Analysis

The temperature at a point removed from the isothermal heat source experiences a delay time ( $t_0$ ) that is dependent on the intervening materials. The initial temperature ( $T_{initial}$ ) is essentially unchanged until this time. There follows a rapid rise which asymptotically approaches a final temperature ( $T_{final}$ ). The ultimate temperature measured by each thermocouple depends on the local thermal environment. The final temperature does not rise to equilibrium with the isothermal

heat source because the system is not adiabatic. Equation (1) below is used to fit the experimental data curves, and includes two measured temperature values, one measured delay time, and one adjustable parameter, the time constant  $\tau$ , measured in seconds. Comparisons between different materials and environments are made based on this characteristic time constant, fitted to the data.

$$T = (T_{final} - T_{initial}) * (1 - e^{-\frac{(t-t_0)}{\tau}}) + T_{initial} \quad (1)$$

Nearly equidistant thermocouples were chosen from each experiment. Distance from the heat source was estimated using the thickness of the Celmet sheets and the thickness of the thermocouple weld junction. The data compared corresponds to TC 8 from Al 550 (19.16 mm), Cu 550 (19.16 mm), and Ni 510 (20.56 mm), and TC 5 from Ni 850 (18.35 mm).

### III. RESULTS

An important factor in making material comparisons for this dynamic system is the degree of silicon particle infiltration into the metal foam matrix. Cross sections of silicon infiltrated nickel Celmet were prepared according to the method presented in Section II.C. Packing density was determined through energy-dispersive X-ray (EDS) analysis. Packing densities of three types of Celmet, Nickel 450, Nickel 510, and Nickel 850, were analyzed with 1-5 micrometer particles and 25-40 micrometer particles. Three scans were taken from each sample, and the ratio of Si:Ni (% mass) measured by EDS was calculated for each scan. To show optimized packing potential, maximum values within the accepted error range (<4.0%) are reported and the results are summarized in Table II.

TABLE II  
 SILICON PACKING DENSITY OF NICKEL CELMET

Celmet Type	Si Particle Size (um)	Si:Ni (% mass)
Ni 450	1-5	0.51
	25-40	0.65
Ni 510	1-5	3.11
	25-40	0.71
Ni 850	1-5	6.19
	25-40	0.57

Nickel 850 provided the highest infiltration ratio of Si:Ni by mass with 1-5 micrometer silicon particles. This sample has the largest size pores in the metal sponge material, and likely allowed easier access for silicon particles. The ratio was drastically reduced with the use of 25-40 micrometer particles, indicating that microspaces in the Celmet foam were less completely filled by the larger silicon particles. Nickel 510 allowed also exhibited a significantly higher infiltration for the smaller particle size. Nickel 450 has the smallest pores and resulted in nearly-equal, and relatively low infiltration results for both silicon sizes.

The sifting technique used to infiltrate the Celmet sheets was intended to minimize clumping of silicon particles. However, once infiltrated, particles appeared to clump again. Larger particles may have a higher clumping factor, further

diminishing infiltration success in all trials. Technique may rely on vibrations internal to the metal foam to motivate the particles to fill up. Aggregating by particle size, trials with 1-5 micrometer particles had an average filling percentage 5.04 times that of 25-40 micrometer particles.

Tests conducted with Aluminum 550 Celmet (thickness 1.0 mm) were used to compare the thermokinetics of systems infiltrated with 1-5 micrometer Si particles versus 25-40 micrometer particles in a 8.5 bar hydrogen environment. After the regular 1500 second test, this test sequence was extended for an additional 1000 seconds to explore asymptotic behavior of temperature. Using (1), the heat constant ( $\tau$ ) was determined to be 700s for the 25-40 micrometer particles, and 650s for the 1-5 micrometer particles. After 2500s, the system packed with the larger particles reached a temperature of 92.86°C (TC9) while the system with smaller particles reached a temperature of 96.1°C. These differences are probably too small to be significant, however, the slightly improved results with the smaller particles (1-5 um) led to their use for all subsequent thermokinetic testing.

The varieties and thicknesses of the Celmet varieties used for thermokinetic testing are: Copper 550 (1.0 mm), Aluminum 550 (1.0 mm), Nickel 510 (1.2 mm), and Nickel 850 (2.4 mm). Trials comparing thermokinetic data of each material were conducted in both vacuum and hydrogen environments. Tests conducted in a vacuum environment indicate results for a completely discharged hydrogen system, while those conducted under hydrogen pressure indicate results for a system at full hydrogen capacity. Hydrogen pressure was maintained at 8 bar [7].

Using (1), the thermokinetics of each trial conducted in vacuum were modeled and used to find the characteristic time constant ( $\tau$ ). Nickel 850, the thickest Celmet foam tested, exhibited the slowest heating rate with a time constant of 640 seconds. Nickel 510 demonstrated a time constant of 630 seconds. Aluminum 550 and Copper 550, the thinnest forms of Celmet tested, exhibited the fastest heating rate with a time constant of 620 seconds. Aluminum with a thermal conductivity of 237 W/(mK) and copper 401 W/(mK) have much better heat conductivity than nickel 90.7 W/(mK) [8]. The systems created with aluminum and copper were equivalent in all aspects aside from the metal used. Even though copper has a higher heat conductivity than aluminum, an aluminum system measured at the same distance from the heat source displayed an identical thermokinetic time constant under vacuum. Nickel 850, with substantially lower thermal conductivity, still exhibited a competitive time constant. The reason for the thicker film to have a similar time constant is believed to be due to having fewer thermocouple-filled spacings between successive layers of metal foam, because of the much-lower thermal conductivity of the silicon particles in between.

Tests conducted in a hydrogen environment produced faster heat kinetics than in vacuum trials, as expected. Time constant values ranged from 450-600 seconds and all cases exhibited faster kinetics compared to a vacuum environment. Nickel 850 showed the greatest kinetic improvement with a time constant of 450 seconds in hydrogen. The other three materials showed

moderate rate increase. The time constant of Aluminum 550 decreased by 20 to 600 seconds, Nickel 510 decreased by 30 to 600 seconds, and Copper 550 decreased by 25 to 595 seconds. A summary of thermokinetic time constants from both vacuum and hydrogen environments is presented in Table III.

TABLE III  
THERMOKINETIC CONSTANTS OF CELMET FOAM

Celmet Type	Thermal Conductivity (W/mK)	T, Vacuum (s)	T, Hydrogen (s)
Al550	237	620	600
Cu 550	401	620	595
Ni 510	90.7	630	600
Ni 850	90.7	640	450

Trials conducted in a hydrogen environment also reached consistently closer to the final temperature of the heat source. These values are summarized in Table IV.

TABLE IV  
FINAL TEMPERATURE COMPARISON

Celmet Type	Final Temperature in Vacuum (C)	Final Temperature in Hydrogen (C)	Temperature Difference
Al550	71.333	95.61	24.28
Cu 550	70.95	102.29	31.34
Ni 510	74.26	94.39	20.13
Ni 850	74.19	97.87	23.68

The 9 cm steel plate acts as a heat sink for the system, and in a hydrogen environment heat is carried by not only conduction through the Celmet but by convection through hydrogen. This is the primary cause behind the faster heat-up in a hydrogen pressure environment.

#### IV. TECHNO-ECONOMIC ANALYSIS

The cost to manufacture and assemble a solid-state hydrogen storage subsystem using the porous silicon and metal foam arrangement is studied to provide a comparison with other forms of storing hydrogen. Because the vehicle market will drive many of the technical requirements, the scale studied is 5.0 kg of hydrogen, suitable for a 500 km range in a passenger fuel cell vehicle. The maximum gravimetric storage of hydrogen on porous silicon is 7.1% w/w. Porous silicon at this level of storage is 80% void space, so the apparent density is 0.418 g/cm<sup>3</sup>. The media volume required for 5 kg of hydrogen relative to an internal combustion engine burning gasoline at a chemical-to-work efficiency 0.5 that of a fuel cell a simple return on investment can be calculated. Assuming long-term gasoline prices of 2.5 USD/gallon and at-scale hydrogen retail costs of 4.0 USD/kg, plus a recharge energy cost of 2.67 USD (Fig. 2), the 10% Celmet-loaded porous silicon hydrogen storage subsystem achieves simple payback after 66,375 miles is 168,000 cm<sup>3</sup> having a fully-charged mass of 84 kg. Because of the 8 bar pressure, aircraft grade aluminum can be used as the vessel wall, adding 19.55 kg [7]. Adding 0.5 kg for controls brings the total storage subsystem mass to 104 kg that, if configured as a cube, has a side length of 55 cm.

The cost to manufacture and assemble a hydrogen storage subsystem based on catalytically-modified porous silicon and Celmet metal foam is dominated by these two materials. Silicon costs, at maturity, are estimated at 7.72 USD/kWh [9], with hydrogen containing 33.3 kWh/kg, or 257 USD/kg for a total of \$1,488. Celmet will add an estimate of \$7,076 if fully-packed into the interior volume. As shown in the experimental data above, this density of foam is not required because the hydrogen gas itself adds thermal convection to thermal conduction. Instead, a 10% loading of Celmet sheets is assumed, spaced every 2.15 times their thickness in all three dimensions. Fig. 2 shows the total manufacturing costs assuming 29.4 USD/hr labor rates per US government rates. The final costs for storage of five kilograms is \$2,374.

The end-of-life (EOL) value depends on the storage capacity after 10 years of vehicle life. Assuming three ignition cycles per day and a recharge needed every five ignition cycles (a conservative estimate), the system is recharged 2,192 times. Assuming hydrogen purity of 99.9999%, with the remainder being oxygen, each recharge reduces capacity by .99999 [10]. The EOL capacity is down 0.978, and assuming remanufacturing of the seals and controls at 35 USD and labor at 1 hour, the value at EOL is estimated as \$2,306.

H <sub>2</sub> Recharge Energy Calculations	
Recharge Pressure	80 N/cm <sup>2</sup>
Recharge volume	168475 cm <sup>3</sup>
Recharge Time	3.5 minute
Energy (=P*V)	1348 J
Power (=E*t)	283 kW
Energy to pressurize	16.51 kWh
Energy cost (US Avg.)	0.15 USD/kWh
<b>COST TOPRESSURIZE</b>	<b>2.48 USD</b>
Recharge Temperature	100 Celcius
Heat capacity	0.71 J/g-K
Ambient Temperature	23 Celcius
Mass of silicon	84069 g
Energy to heat	4596053 J
Energy units	1.277 kWh
<b>COST TO HEAT</b>	<b>0.192 USD</b>
<b>TOTAL RECHARGE COST</b>	<b>2.67 USD</b>

Fig. 2 Energy Costs to recharge a porous silicon based hydrogen storage system

#### V. DISCUSSION

Nickel 850 continually outperformed other materials tested in both infiltration and heating kinetics. The structure of Nickel 850 demonstrates several characteristics of a successful system including large pores, minimized number of nickel cells per area, and thick sheets to minimize gaps that must be bridged between the metal sheets. Due to the fewer number of sheets used in the Nickel 850 experiments, its also noteworthy that the gaps that are created maintain a smaller percentage of the total distance heat travels. Minimizing gaps between the conducting structure, or a seamless metal framework may further improve kinetics of heat distribution. A material with a higher thermal conductivity, such as copper or aluminum, may provide an even

greater increase heating rate for cases where the hydrogen storage is in a nearly-empty state.

COSTS for 5.00 kg HYDROGEN STORAGE VESSEL with Celmet at 10%							
Materials	porous silicon	7.72 USD/kWh	33.3 kWh/kg	257 USD/kg	5.79 kg	\$ 1,487.99	
	Celmet	0.14 g/cm <sup>3</sup>	2.358 kg	estimate		\$ 707.59	
	Vessel	3.586 USD/kg	19.55 kg	<a href="https://gmetalminer.com">https://gmetalminer.com</a>		\$ 70.09	
	Controls	Flow controller, relay, computer		estimate		\$ 35.00	
Labor	Forming	0.5 hours	29.4 USD/hr	<a href="https://www.bls.gov/">https://www.bls.gov/</a>		\$ 14.70	
	Welding	1.2 hours	29.4 USD/hr	<a href="https://www.bls.gov/">https://www.bls.gov/</a>		\$ 35.28	
	Assembly	0.6 hours	29.4 USD/hr	<a href="https://www.bls.gov/">https://www.bls.gov/</a>		\$ 17.64	
	Finishing	0.2 hours	29.4 USD/hr	<a href="https://www.bls.gov/">https://www.bls.gov/</a>		\$ 5.88	
At 10%, Celmet sheets spaced every 2.15 times their thickness						<b>TOTAL</b>	\$ 2,374.17

Fig. 3 Manufacturing costs for 10% loading of Celmet™ sheets in 5.0 kg hydrogen storage vessel

## VI. CONCLUSION

The experimental data indicate that at depths of 1.2 cm from an external heat source, the thermal response of a hybrid porous silicon-metal foam storage media has a time constant of approximately 600 seconds when nearly empty, and 450 seconds when nearly full. For a FCV application, this hydrogen storage system will require either an intermediate surge reservoir, or a shorter distance between heater and interior storage material. The presence of the Celmet™ metal foam significantly improves thermokinetic performance, and is also expected to reduce settling of the silicon particulates. Because hydrogen convection is an important contributor to thermal response, this avoidance of settling is a beneficial feature in achieving rapid discharge of hydrogen by using Celmet metal foam in a solid-state hydrogen storage system.

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