

NANOPOROUS SILICON BASED ENERGETIC MATERIALS

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1. BACKGROUND

Energetic materials are an important component of military defense systems and are used in applications ranging from explosives to gun and missile propulsion. Energetic materials are used in a number of critical defense components ranging from shaped charges, actuators, and delay lines to detonators. U.S. defense needs for advanced energetics have been evolving rapidly in recent years. The need for increased mobility, enhanced range and lethality, reduced or modified signatures, reduced collateral damage, and the capability to destroy hardened and buried targets has increased demand for enhanced energetic materials (NRCReportt2004). Nanoscale materials have been instrumental in the development of new energetic materials with novel properties. Energetic materials that are produced on the nanoscale have the promise of increased performance in a variety of ways. Metastable Intermolecular Composites (MICs) belong to a class of nanoscale energetic materials that have been extensively studied. (Subramaniam et al 2006, Son et al 2006, Granier et al 2004, Tillotson et al 1998, Tillotson et al 2001).

MIC formulations are mixtures of nanoscale powders of reactants that exhibit thermite (high exothermicity) behavior. The main difference from more traditional energetics is that the reactivity is based on intramolecular (not intermolecular) properties. The MIC formulations are based on intimate mixing of the reactants on the nanometer length scale, with typical particle sizes in the tens of nanometers range (e.g. 30 nm). One important characteristic of MICs is the fact that the rate of energy release can be tailored by varying the size of the components. (Miziolek 2002). Possible applications for these materials include use in environmentally clean primers and detonators, chem/bio agent neutralization, improved rocket propellants, IR flares/decoys, high temperature stable, non-detonable gas generators and thermal batteries.

Porous Si (PSi) is a sponge-like form of silicon usually produced by anodic etching of single crystalline Si wafers in hydrofluoric acid solutions. The etching process results in the formation of pores, which can range from macropores to mesopores, depending on the

etching conditions. The porous structure leads to a high surface area material and hence increased reactivity. Porous Si has been explored as an energetic material and reactions with strong oxidizers such as metal nitrates have been observed (Clement2005, Mikulec 2002). PSi is also being considered for primary explosive applications as a “green alternative” to lead azide based systems. In addition to energetics, applications for PSi include electrodes for Li ion batteries, precursor for ceramics for armor applications, hydrogen storage, biomedical applications and catalysis, all of which have numerous applications in the military. The synthesis of porous Si through electrochemical etching is an expensive route due to the cost of single crystalline silicon substrates and is difficult to scale –up. The morphology of porous Si formed via electrochemical etching is as a thin film on a substrate, which requires additional steps to create particles.

Vesta Sciences has developed a process for producing low cost porous Si from metallurgical grade silicon powders through a chemical etching process. The etching process creates a network of nanocrystals with very fine porosity of 4 - 5nm within the micron-sized particle. These are therefore, **nanostuctured** materials. In this paper, the synthesis of these novel materials will be described and results from characterization techniques such as scanning and transmission electron microscopy will be presented. The energetic properties on incorporation of various oxidizers will also be described.

2.EXPERIMENTS

2.1. Synthesis of PSi particles

PSi particles were prepared by stain etching of bulk metallurgical grade silicon powder from Vesta Ceramics which is sold under the trademark of Sicomill™. Vesta Ceramics Sicomill™ is available in two grades of composition (Grade 2 has a higher impurity level than Grade 4) and multiple grades of particle size. The particle size distributions as measured by laser diffraction show a d_{50} of 4, 7, 11microns for E, D, C grades respectively. These powders were etched in a nitric acid- hydrofluoric acid mixture as described in Farrell 2007. After the etching process was complete,

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the etched powder was removed from the acid bath and dried in PFA trays at 80C for 24h. The B.E.T. surface area of the powders was measured by nitrogen gas adsorption in a Micromeritics Gemini V gas adsorption analyzer. The pore size distribution and pore volume were estimated by using the Barrett-Joyner-Halenda Scheme. The particles were also characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction. By varying the nitric acid concentration in the etchant mixture the surface area of the powders could be tailored. Since surface area is expected to be the primary factor affecting reactivity, the powders can also be tailored for different applications.

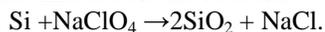
2.2. Oxidizer incorporation

Several methods were used to incorporate oxidizers into the pores of the PSi particles. These can be broadly classified into

- 1: solution methods where the oxidizer is either dissolved or dispersed in a solvent
- 2: mixtures where the oxidizer is mixed with the powders either ultrasonically or by other methods.

Oxidizer incorporation into the pores of particles with high surface area is expected to have the highest reactivity. To incorporate oxidizers in to the pores, methods similar to those described in Clement et al 2005 for electrochemically etched porous Si layers were used. PSi powders are hydrophobic as a result of a H-terminated surface after etching in HF solutions. This necessitates using organic solvents for wetting the pores.

As an example, sodium perchlorate was dissolved in dry methanol to give a 50 wt% solution. Appropriate amount of the solution was added to PSi powders to give a stoichiometric mixture for the reaction



and the solvent was allowed to evaporate. The powders were further dried at 60C in vacuum drying oven for 4 to 6 hours.

For oxidizers that are not soluble in organic solvents, mixtures of PSi and oxidizers such as potassium nitrate and potassium perchlorate were prepared by gently mixing stoichiometric amounts together in milligram quantities.

One of the applications explored for this material was as a tunable thermite and for this reactions with metal oxides were investigated since these give high heats of reaction. Two approaches were undertaken for this:

1. Sol-gel synthesis of iron oxide within the pores of the PSi particles
2. Mixtures of nano-copper oxide and PSi by ultrasonic methods

The goal of the sol-gel synthesis was to form iron-oxide particles within the pores. For this, methods similar to those described by Gash et al to form iron oxide aerogel and xerogels were used (Gash 2001). This method has been used to form energetic composites with nano aluminum particles (Tillotson 1998). In the first experiment, 1g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 5g of 200 proof ethanol in a beaker to give an orange solution. To this 1.0 propylene oxide was added to yield a reddish brown solution that indicates the formation of iron oxide. A measured amount of PSi was stirred in and the solution was allowed to gel slowly as the solvent evaporated. This process resulted in the formation of a reddish brown powder when all the solvent was evaporated. The powder was further crushed in an agate mortar.

The as-prepared iron oxide-PSi powders yielded higher than stoichiometric weight which is likely due to retained solvent. The powders were further heated at 350C in a furnace under flowing nitrogen to remove any residual solvent.

For forming PSi-copper oxide mixtures, a mixture of PSi with nanocrystalline CuO ((31nm, 32m²/g surface area) and nanocrystalline Bi₂O₃ from Nanophase Technologies (38nm, 18m²/g surface area) was created by dispersing 25mg of a 2:1 molar ratio CuO-PSi in 10ml of hexane. The solution was sonicated for 10 minutes and the hexane evaporated.

2.3. Testing of Energetic Properties.

PSi- oxidizer mixtures were tested for ignition by thermal methods at various temperatures up to 350C. PSi-iron oxide mixtures were difficult to ignite at low temperatures and were heated in a low temperature furnace in flowing nitrogen to various temperatures to check for reactions. The reaction rate of PSi- sodium perchlorate infiltrated powders was measured by detecting the start and end of the reaction by short circuit of a twisted cable at the entrance and exit of a chamfer in a steel plate (Clement personal communication). Burn rate of PSi-oxidizer mixtures were measured in open burn tests using a high speed video camera (Clement, personal communication). Electrostatic discharge sensitivity of PSi-NaClO₄ mixtures were tested using a ESD simulator as described in section 3.3.

3. RESULTS AND DISCUSSION

3.1. Porous Silicon Synthesis and Characterization

PSi powders were prepared from various grades of metallurgical grade silicon powders as described in Section 2.1. The initial step of this reaction is proposed

to be the reduction of HNO₃ and injection of holes (h⁺) into the valence band of silicon (Lehmann 2002)



The injected holes are consumed in the dissolution reaction as below



The final dissolution product is a tetravalent hexafluoride complex (SiF₆²⁻). The majority of the gas that evolves during silicon dissolution is hydrogen with some amount of N₂O and traces of NO and NO₂. The reduction of HNO₃ is autocatalytic and goes through an induction period where the buildup of HNO₂ increases the etching rate to a steady state value (Lehmann 2002). The formation of nanocrystals within the larger Si grains due to the formation of pores results in bright orange-red emission from the powders under UV illumination. This indicates that the nanocrystals formed within the micron size Si powder are so small that quantum confinement effects start to play role (Canham 1990). The bandgap of nanoparticles becomes larger and shifts from the infrared to the visible and results in the red-orange emission. The etching process is monitored and stopped when luminescence is observed from the powders under UV illumination. This results in powders with the highest surface area but since the porosity is very high, the yield of the powder is low. For lower surface areas, the reaction can be stopped at lower levels of porosity by adjusting the amount of nitric acid added. Table 1 is a summary of surface area, pore volume and pore size of various grades of porous Si prepared by this method.

Table 1 : Summary Of Properties Of Porous Si Powders

Silicon grade	Particle Size (μ)	Nitric Acid concentration (%)	B.E. T. Surface Area m ² /g	Mean Pore Size (Å)
PSiE1	4	2.0	41	8.1
PSiE2	4	2.7	82.55	6.6
PSiE3	4	3.4	143	4.98
PSiD1	7	2.0	60	6.3
PSiD2	7	2.7	97	5.9
PSiD3	7	3.4	130	5.3
PSiC1	11	2.0	56.3	6.17
PSiC2	11	2.7	65	6.6
PSiC3	11	3.4	128	4.95

This shows that the surface area of PSi powders can be varied from that of bulk silicon powders (~ 4 m²/g) to ~ 150 m²/g. The E3 grade of porous silicon was

investigated in detail since it has the highest surface area. The powders were examined by X-ray diffraction and found to be crystalline. Figure 1 shows a SEM image of an E3 grade PSi particle. The surface of the particle appears porous with pores in the range of microns. This is larger than the 5 nm average pore size measured by gas adsorption and may indicate a gradation in pore size from the surface to the center of the particle. Figure 2 is a low magnification bright field TEM image and shows a porous sponge like structure. High resolution TEM images show nanocrystals of silicon within the larger particles with interspersed porosity (Figure 3).

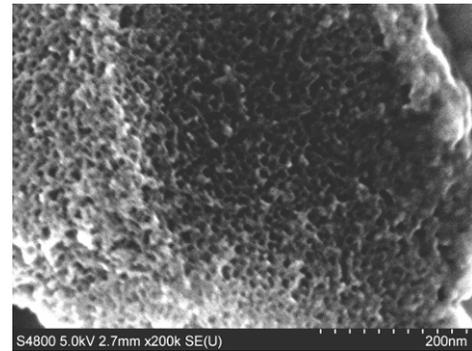


Figure 1. High resolution SEM image of PSi surface showing pores in the 10 nm range (Univ of Limerick)

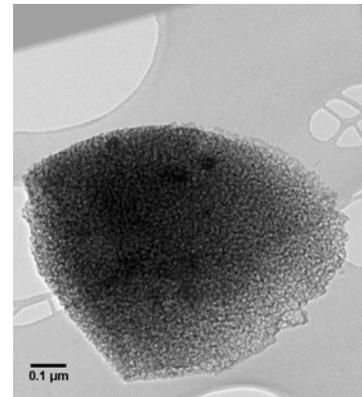


Figure 2. Bright Field TEM image of PSi particle showing sponge like structure (Univ of Limerick)

The surface of porous Si particle is terminated with Si-H and H-Si-H bonds. This renders the surface hydrophobic and stable against aging in humid environments. The lack of an oxide passivation layer results in nearly all the silicon being available for reaction as opposed to Al based systems where the oxide layer reduces the reactive metal available. The Si-H termination is seen on the as prepared 4E grade PSi sample in the results from Diffuse Reflectance Infrared Spectroscopy (DRIFTS) experiments performed at SINTEF, Norway as shown in Figure 4 (line a).

Annealing PSi in air at different temperatures can be used to change the surface termination. Hydrogen is effused from the surface of silicon at $\sim 300\text{C}$ leading to oxidation at the surface. Therefore annealing at temperatures above 300C leads to appearance of strong Si-O bonds and the Si-H bands disappear as seen in Figure 4 (line c). Annealing at a temperature of 150C leads to the formation of backbonded oxygen, while maintaining the Si-H termination as seen in Figure 4 (line b). The backbonded oxygen layer lends significant surface stability to the material against aging. The reactivity of the material decreases as the level of oxidation increases and can be used to tailor it. The stability of the material was also checked by comparing the level of oxidation on as-prepared E-3 grade sample after 1 year of storage under ambient conditions by X-ray Photoelectron Spectroscopy (XPS). These results did not indicate significant changes in oxidation level suggesting that the surface is stable against oxidation. Partial or complete oxidation of the surface can also render PSi-oxidizer mixtures less sensitive to friction and impact.

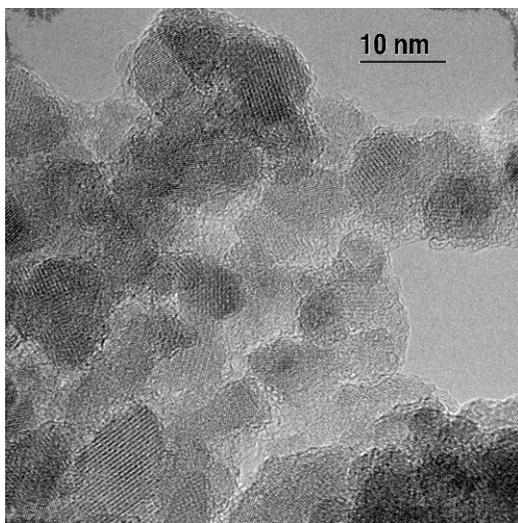


Figure 3 High resolution TEM image showing Si nanocrystals (3-4 nm) with interspersed pores. Si $\langle 111 \rangle$ fringes are observed. (courtesy Dr. Howe, ORNL)

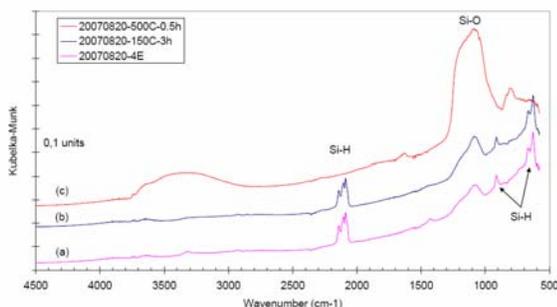


Figure4 DRIFTS spectrum showing Si-H and Si-O bonds from (a)as-prepared PSi, (b)PSi heated to 150C for 3h (c)PSi annealed at 500C for 0.5 h (courtesy SINTEF)

3.2. Characterization of porous Si- iron oxide composites prepared by sol-gel methods.

To investigate the extent of penetration of Fe_2O_3 in to the pores, the PSi-iron oxide composites were examined by X-ray diffraction, SEM and TEM. X-ray diffraction showed that the as-prepared material is amorphous. Heating the as-prepared powders to 300C under nitrogen for 1h resulted in a weight loss and crystallization of the powder. X-ray diffraction showed a mixture of maghemite and PSi after the low-temperature anneal. SEM images suggest a particle size of ~ 4 microns which is consistent with the mean starting particle size of the silicon powder. Energy Dispersive X-ray Analysis in the SEM shows the presence of both iron and Si within the particle.

To investigate the distribution of iron oxide within the PSi particles, transmission electron microscopy (TEM) was carried out. A small sample was heated at a low temperature under nitrogen to remove the solvent and crystallize the iron oxide. The sample was embedded in an epoxy and microtomed to obtain thin sections. These were suspended on a holey carbon grid for examination in the TEM.

TEM studies were carried out under the USER-SHARE program at Oak Ridge National Laboratories by Dr. Jane Howe on a Hitachi HF2000 TEM. Figure 5 is a low magnification image: the inset electron diffraction pattern from region indicates the presence of both PSi (spots) and the rings correspond to the maghemite phase, consistent with the X-ray diffraction analysis. Annular Dark Field images taken in the STEM showed bright areas corresponding to areas where iron oxide is dominant and dark areas corresponding to lower amounts of iron oxide. This was also confirmed using Energy Dispersive X-ray Analysis in the STEM. From this analysis it appears that while most of the iron oxide is present on the outside of the PSi particles, there is some penetration into the pores. These results suggest that a fairly intimate mixing between the iron oxide and PSi is achieved.

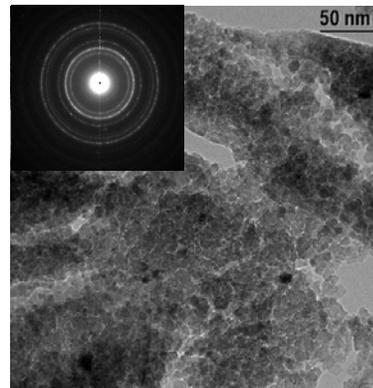


Figure 5: Lower magnification bright field TEM image of PSi- Fe_2O_3 . The inset electron diffraction pattern shows rings from the maghemite phase and spots from PSi (image recorded by Dr. Jane Howe at ORNL)

3.3 : Energetic properties

3.3.1 : Reactions with strong oxidizers

The theoretical heats of reaction of Si with various oxidizers are summarized in Table 2. From this table, it is evident that the highest heat of reaction/ g of reactants is observed for strong oxidizers such as sodium perchlorate and potassium perchlorate.

Table 2: Estimated Heat of Reaction with Oxidizers

Reaction	ΔH_r (kJ)	ΔH_r (kJ/g)
$\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$	-857	-15.2
$2\text{Si} + \text{NaClO}_4 \rightarrow 2\text{SiO}_2 + \text{NaCl}$	-1737	-10.4
$2\text{Si} + \text{KClO}_4 \rightarrow 2\text{SiO}_2 + \text{KCl}$	-1718	-9.4
$5\text{Si} + 4\text{KNO}_3 \rightarrow 5\text{SiO}_2 + 2\text{N}_2 + 2\text{K}_2\text{O}$	-3019	-6.1
$\text{Si} + (\text{C}_2\text{F}_4)_n \rightarrow \text{SiF}_4 + 2\text{C}$	-806	-6.2
$3\text{Si} + 2\text{Fe}_2\text{O}_3 \rightarrow 3\text{SiO}_2 + 4\text{Fe}$	-905	-2.2
$\text{Si} + 2\text{CuO} \rightarrow \text{SiO}_2 + 2\text{Cu}$	-567	-3.5
$\text{Si} + \text{Bi}_2\text{O}_3 \rightarrow \text{SiO}_2 + \text{Bi}$	-1423	-1.4

Sodium perchlorate is the most efficient oxidizer for the system since it has a high solubility in methanol and can be relatively easily incorporated into the pores of the oxidizer (180mg/100mg , ref. Clement et al 2005) . The energy yield as measured from bomb calorimetry experiments is ~ 8.1 kJ/g. The reaction velocity of this system was measured by placing the PSi- NaClO₄ in a chamfer in a steel plate, igniting at one end with a standard igniter and measuring the reaction time by short circuit of a twisted cable placed at the entrance and exit of the chamfer. The reaction velocity measured using this method for PSi-E3 grade material with a surface area of 150 m²/g was 2484m²/s for fully dried samples. (Clement personal communication). The open burn rate of PSi-KClO₄, PSi-Pb₃O₄ and PSi-KNO₃ physical mixtures were measured by filling a chamfer of known length. The mixture was ignited from one end the reaction time was estimated from high speed video. The results of the reaction rates for oxidizers tested thus far are documented in Table 3.

3.2: Reaction with metal oxides

The reactions of PSi-E3 grade material with iron oxide incorporated by sol-gel methods described in section 2 and those of PSi- nano CuO and PSi- nano Bi₂O₃ from Nanophase materials was investigated. Nanothermites have conventionally used nano Al as the metal since Al has a low melting point and the heat of reaction with metal oxides is high. The heat of reaction

for Si with metal oxides is slightly lower than that of Al. However, the melting point of Si is much higher at 1410C, which makes it difficult to initiate reactions.

Table 3 : Reaction Rate of PSi with Oxidizers (Clement personal communication, 2008)

Silicon Type	Oxidizer	Estimation of Burn Rate/Reaction Rate
pSi-E3	KClO ₄	100 cm/s
pSi-E3	KNO ₃	50 cm/s
pSi-E3	Pb ₃ O ₄	2 cm/s
pSi-E3	NaClO ₄	2484 m/s

The sol-gel iron oxide-PSi composite were found to be difficult to ignite though heating above 1200C was found to result in a thermite reaction with the formation of silica and iron. Nanophase copper oxide and bismuth oxide were tested to see if some incorporation of nanooxides into the pores would lead to a higher reaction rate. This was found to be successful with both CuO-PSi mixtures and Bi₂O₃-PSi mixtures undergoing ignition with a flash. Qualitatively, the reactions are slower than those with stronger oxidizers such as nitrates but the reaction of PSi-Bi₂O₃ is comparable to nano aluminum-nano iron oxide thermites. Figure 6 and Figure 7 show the ignition of PSi-nano CuO and PSi-nano Bi₂O₃ powders.

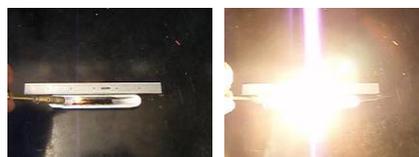


Figure 6 Frames from the ignition of PSi-nano CuO powders (courtesy, Dr. Puszynski and Chris Bulian South Dakota School of Mines)

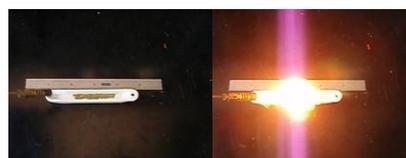


Figure 7 Frames from a video of the ignition of PSi-bismuth oxide ((courtesy, Dr. Puszynski and Chris Bulian South Dakota School of Mines and Technology (SDSMT))

3.3. Electrostatic discharge (ESD) sensitivity measurements

ESD sensitivity tests were carried out on the PSiE3-NaClO₄ system by Chris Bulian and Dr. Jan Puszynki at the SDSMT). NaClO₄ was incorporated into the pores using solution methods as described in Section 2. . The material was easily ignited by flame and exploded when heated uniformly by flame in small caliber primer cups. A Model 930D-FTS Electrostatic Discharge Simulator from Electro-Tech Systems, Inc was used for the ESD tests. The procedure was in accordance with military standards where the sample is subjected to 20 consecutive discharges at a particular energy level. If no ignition occurs, the discharge energy is increased and 20 consecutive tests are again completed. The material was tested both as a powder and as a thin film on a metal disc. In both cases, the discharge energy up was increased to 25 mJ without having any ignition of the material. These preliminary results suggest that the ESD sensitivity of this material is much lower than nanothermite systems based on aluminum.

3.4 Shaping of PSi powders

It is also possible to fabricate flexible tapes, sheets, wires, etc. from PSi using a PTFE fibrillation process. PSi powders are mixed with Dupont No.60 Teflon™ powders in a solvent to form a paste. The mixture is extruded through rollers to form a sheet. This technology allows the fabrication of shaped articles from the powders while preserving the porosity and surface area. The oxidizer if in solution can be added after the fabrication of the tape, improving the ease of handling and safety aspects. Figure 8 shows a picture of such a tape. Alternatively, the solid oxidizer can be added to the powders prior to forming the tape and the mixture extruded.

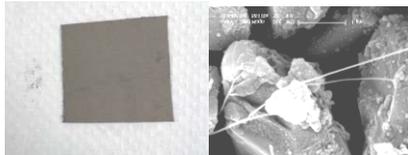


Figure 8: Flexible tape fabricated from PSi powders. SEM image showing particles encased in a mat of teflon fibers.

A tape fabricated from PSi-E3 grade material was infiltrated with sodium perchlorate methanol solution. Ignition produced a fast reaction rate comparable to that of the powder with sodium perchlorate.

4. SUMMARY

Porous silicon powders of varying surface area, porosity and reactivity can be synthesized from

metallurgical grade silicon by chemical etching in HF-HNO₃ solutions. The porous structure results in the formation of nanocrystalline grains with the micron size silicon particles along with pores in the range of 5 to 10 nm. This nanostructured material is highly reactive and can form a highly energetic material when combined with an oxidizer. The most efficient oxidizers giving rise to the highest reaction rate were those that could be incorporated into the pores of the particles in solution form. Energetic reactions were also observed when physical mixtures of PSi with other oxides such as metal oxides were formed. PSi surface is hydrogen terminated and is expected to be stable against aging effects that lead to oxidation and decrease in the reactive metal available. PSi- sodium perchlorate mixtures were found to be relatively insensitive to ESD despite being highly reactive. The properties of this material suggest that there is great potential for its use in energetic applications.

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