Sodium Silicide—A New Alkali Metal Derivative for Safe, Sustainable and On-Demand Generation of Hydrogen

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Category/Focus: Small Business Category and Focus Area 3: Design of Greener Chemicals.

Recent Milestone: In February 2011, SiGNa Chemistry signed a licensing agreement with myFC, a Swedish-based fuel cell company. This agreement allows myFC to use sodium silicide as the hydrogen-generating technology for their fuel cell products. The company's first NaSi-powered product is the PowerTrekk™, a portable hydrogen charger. PowerTrekk™ is available now in Europe and beginning in April 2012, a leading sporting goods retailer will distribute the PowerTrekk™ charger and PowerPukk™ refillable cartridges at more than 120 U.S. outlets.

Regional Technology Development: Sodium silicide technology was developed and commercialized entirely within the United States.

Abstract: Sodium silicide (NaSi) is a stabilized alkali metal silicide powder that reacts with any water solution to instantly generate hydrogen. SiGNa's NaSi powder is a patented new composition of matter, where its molecular structure has been modified according to its novel X-ray diffraction pattern to delocalize the electrons across the clathrate, forming an air-stable free flowing powder.

When used in a fuel cell, NaSi produces pure hydrogen gas in real time, as needed by the fuel cell, and at pressures less than those found in a soda can. NaSi overcomes the most significant challenges that have prevented low-temperature proton exchange membrane (PEM) fuel cells from becoming commercial products, specifically the need to store high-pressure hydrogen and build a costly hydrogen refilling infrastructure. This clean, sustainable material is inexpensive, easily transportable, and safe for indoor use. Fuel cells powered by NaSi produce only hydrogen and water vapor; they create no greenhouse gases, toxic by-products, or harmful emissions. Recyclable fuel cartridges can easily deliver NaSi to any PEM fuel cell; once the NaSi in a cartridge is spent, a non-toxic, environmentally benign residue can be recycled as an industrial feedstock for other products.

SiGNa's NaSi technology offers significant environmental benefits throughout its lifecycle. NaSi is manufactured using renewable and sustainable materials that are independent of oil prices. The manufacturing process requires little energy and has a very small carbon footprint. Replacing lithium batteries and internal combustion (IC) engines with NaSi fuel cells can reduce greenhouse gases released into the atmosphere by nearly 14% and significantly reduce the amount of toxic materials entering the waste stream.

SiGNa's novel hydrogen-storage approach can enable cost-effective back-up and portable fuel cells for the medical, military, transportation, disaster relief, and consumer electronics industries. This technology is proving that hydrogen fuel cells are not only commercially viable, but even more high-performing and cost-effective than batteries or low-power IC engines (under 3 kilowatts). For example, NaSi can replace the combustion engines/gas back-up in battery-hybrid cars to extend its range by 50 miles or an e-bike powered by NaSi can go 3–4-times farther than a bicycle powered by lithium-powered batteries.

PROBLEM TO BE ADDRESSED

The storage of pressurized hydrogen gas continues to be the most significant technical challenge preventing the widespread acceptance of hydrogen fuel cells. Yet all commercially-available hydrogen fuel cells and demonstration projects rely exclusively on high-pressure storage tanks or metal hydrides. These conventional approaches not only create safety and hydrogen control management issues, but in most cases, they require the development of a costly infrastructure to refill hydrogen tanks. Sole reliance on pressurized hydrogen tanks has, and will continue to, severely limit the expansion of hydrogen energy.

To overcome this technical challenge and spark a near-term growth of hydrogen energy, SiGNa Chemistry has developed a new stabilized alkali metal powder (NaSi) that produces pure hydrogen from water. This powder and its derivatives generate hydrogen reliably and on-demand; they also overcome the safety and cost issues that have plagued the fuel cell industry since its inception. With consumer products on the market now, NaSi is proving that hydrogen fuel cells are a commercially-viable, cost-effective and realistic energy alternative.

1. SCIENCE AND INNOVATION

Sodium Silicide

NaSi is a new chemical molecule that harnesses the energy potential in alkali metals and silicon. Now a non-flammable, air stable powder, SiGNa's NaSi instantly reacts with water (or any water solution) to form pure hydrogen. This molecule is created through the reaction of sodium metal with silicon powder and it yields significantly more hydrogen per weight than pure sodium or stabilized alkali metals. Unlike sodium, however, it is non-pyrophoric, non-oxidizable, and non-flammable. It also differs from other hydrogen-generation materials in that no hydrogen is actually stored in the NaSi, therefore NaSi's long-term storage is not an issue.

As shown in Figure 1, NaSi differs markedly from the prior known and published NaSi. Using SiGNa's novel low-temperature process to stabilize alkali metal materials, the delocalization of the alkali metal's electrons was able to be maintained to form a never-before-seen NaSi crystal structure. This new composition was patented in U.S. Patent # 7,811,541.

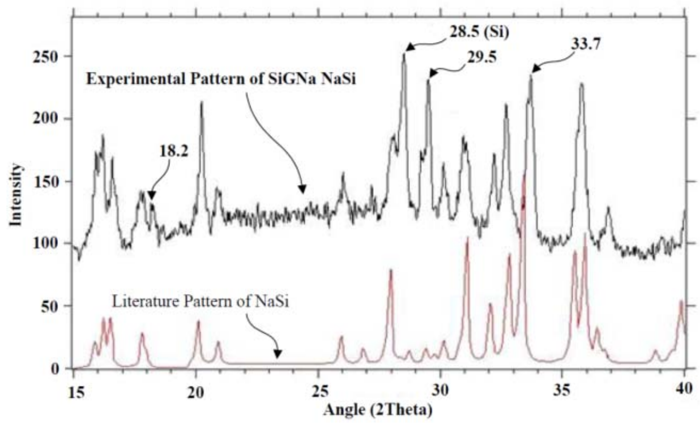

Figure 1. Literature NaSi molecule XRD pattern compared to SiGNa's NaSi.

SiGNa's NaSi process is also performed at several hundreds of degrees Celsius lower than the known process for prior NaSi compositions. The electron delocalization drives novel properties to the NaSi that were not believed to be possible for such a pyrophoric and unstable inorganic material.

SiGNa's NaSi is an air-stable, free flowing powder that reacts instantaneously with any water solution to produce molecularly clean hydrogen gas on-demand. NaSi has been shown to readily and controllably react with water, liberating pure hydrogen. NaSi's reaction with water produces 2.5 moles of hydrogen according to the reaction

$$2NaSi(s) + 5H_2O(\ell) \rightarrow 5H_2(g) + Na_2Si_2O_5(aq)$$

Sodium Silicide/Sodium Borohydride Hybrids

For ultra-high-performance, energy-dense applications, SiGNa has also developed a sodium silicide/sodium borohydride ($NaSi/NaBH_4$) hybrid. This hybrid is a lightweight powder that is high in gravimetric energy density and can store >15.5 wt% hydrogen on a solid basis and >6.5 wt% on a total chemical basis (including water). The hybrid is air stable, non-flammable, and thermally stable. It does not react with oxygen nor decompose by heat under storage, and it does not require a catalyst to generate hydrogen, like pure $NaBH_4$ systems for the fuel cell.

Previous demonstration projects have attempted to use $NaBH_4$ alone to power fuel cells. These projects have shown that $NaBH_4$ does achieve a relatively high energy density, but the resulting fuel cell systems are overly complex and exhibit poor reliability. Systems that use $NaBH_4$ in a liquid solution suffer from numerous fuel stability problems. Borate crystals tend to form in the fuel causing check valve sealing issues. In addition, the hydrogen tends to self-liberate with time and temperature under storage conditions.

SiGNa's NaSi/$NaBH_4$ hybrid combines the best of both chemicals: high-energy density from the $NaBH_4$ with the instantaneous kinetics from the NaSi. As a result, the hybrid enables a water-activated system that is time and temperature stable. Hydrogen is first generated by adding water and reacting the NaSi. The NaSi in the hybrid then acts as a catalyst and promotes the thermolysis of $NaBH_4$. The hybrid will not activate until a water solution is introduced. The NaSi provides a near instantaneous reaction with water generating hydrogen while the $NaBH_4$ provides hydrogen once the reaction has reached its internal control temperature. This approach overcomes the technical issues experienced for the last decade with chemical hydride fuel systems by combining the best features of hydrolysis and thermolysis chemistry to enable low complexity, high-density fuel cell systems like never before.

Low-complexity and highly-reliable fuel cells

NaSi and its hybrids can power any low-temperature PEM fuel cell application needing <3kW of power. The NaSi and NaSi/$NaBH_4$ "fuel" is stored in recyclable cartridges that facilitate easy to use, low-cost, and low-complexity fuel cell systems (compared to other high-density hydrogen-generation materials like sodium borohydride or ammonia borane). Because NaSi and its hybrids are solid and non-flammable, these canisters are also inherently safer than other hydrogen storage alternatives. For instance, a comparable compressed hydrogen system stores flammable gas at >4,000 psi (276 bar).

For fuel cell manufacturers, the advantages of the NaSi-based fuel cell systems include:

- **Hydrogen produced on demand**. No pressurized, flammable gas is stored in NaSi.
- **Fast startup capability**. System startup in less than 5 seconds without hybridization.
- **Independent orientation**. Fuel cells can operate in an orientation independent fashion.
- **Continuous start/stop capability**. Fuel cells can start and stop throughout cartridge life.

SiGNa has designed several types of NaSi cartridges (see Table 1), which are capable of yielding up to 600 standard liters of hydrogen in a size of 3.5" diameter by 9" (~1.4 liters).

2. INNOVATION—CLEAN AND SUSTAINABLE ENERGY

Some believe that hydrogen will never become a mainstream source of electricity. These critics argue that it is too costly to produce, store and distribute pressurized hydrogen gas. By taking a new approach, however, SiGNa has developed a radically different generation process that has resulted in a sustainable, clean and cost-effective source of hydrogen gas. This innovative green chemistry can be the crucial bridge away from U.S. dependence on fossil fuel energy.

Table 1. NaSi and NaSi/$NaBH_4$ canister options.

	H-10 Canister	H-40 Canister	H-800 Canister
Power	0 to 5 W	6 to 50 W	50 to 500 W
Capacity	10 Hrs	> 40 W-Hrs	800 W-Hrs/Canister
Volume	22 c	1.6" X 3.5"	3.5" X 9" / Canister
Pressure	3 psi for regulator-free fuel cell	~15 psi	~30 psi
Design Features/ Architecture	-Passive -Water Self-Contained -Orientation Independent -Start/Stop Capable	-Passive -Water Self-Contained -Orientation Independent -Start/Stop Capable	-Pump-driven -Water Fill Port -Start/Stop Capable
			

Energy-Efficient and Cost-effective Manufacturing Process

To realize the environmental and energy benefits that hydrogen offers, the production of hydrogen gas cannot continue to rely on fossil fuel power. Existing hydrogen production technologies are costly and require fossil fuels. Nearly half of all hydrogen produced today uses natural gas, with another 20% coming from coal. These production techniques not only continue our use of fossil fuels, but they are extremely inefficient processes whereby a significant portion of energy is lost as waste heat. NaSi and its hybrids eliminate the need to produce hydrogen gas.

The process to manufacture NaSi and NaSi/$NaBH_4$ is straightforward and inexpensive. NaSi is formed by combining sodium metal with silicon powder. The primary materials (sodium and silicon) are both abundant and renewable materials whose prices are not influenced by the cost of oil and are available globally. For every 1 kg of NaSi produced, the combined raw materials cost is less than $4/kg. The purity of the raw materials is also not a factor in the creation of NaSi and the manufacturing process is clean. Every ingredient that goes into the reactor ends up in the final product and there are no solvents, crystallizations steps, or purification.

Clean and Sustainable Energy

With NaSi, hydrogen energy is clean and sustainable. The energy created by NaSi fuel cells generates zero greenhouse gases, no toxic by-products, and no harmful emissions.

The energy efficiency advantages associated with NaSi and NaSi/$NaBH_4$ are partly derived from the production of the primary raw material (sodium), which is produced in the U.S. using hydropower. NaSi has been shown to have a carbon footprint that is 90% lower than other chemical hydrides used for fuel cells. One of the world's largest dry cell battery manufacturers conducted a study to estimate the carbon footprint and greenhouse gas emissions associated with the manufacture of four fuel cell and battery chemicals: NaSi, perhydro-N-ethylcarbzole, sodium borohydride and perhydro-fluorene.[1] The goal was to determine which chemistry is environmentally preferable. As seen in Figure 2, NaSi was determined to have the lowest carbon footprint as it uses less energy-intensive raw materials (i.e., sodium produced using hydropower) and processing. The silicon contributed 81% of the total carbon footprint of this chemistry, so lower impact sources, like recycled electronics, are being investigated.

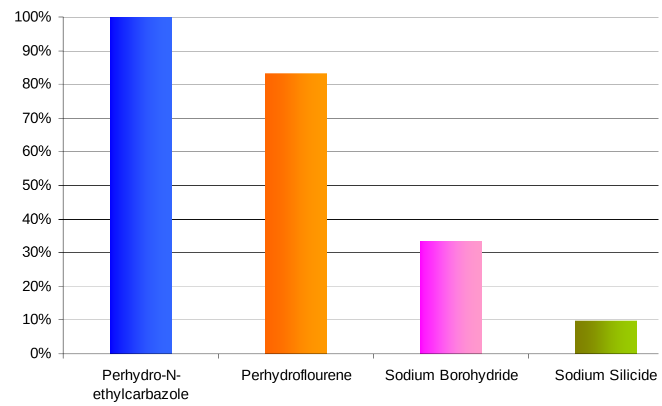

Figure 2. Results of LCA carbon footprint study.

Fully Recyclable Energy Technology

Once the NaSi or NaSi/$NaBH_4$ in a fuel cartridge is spent, the fuel cell is left with a non-toxic by-product called sodium silicate ($Na_2Si_2O_5$). Sodium silicate, often called "water glass", is a common industrial material that is used as an industrial feedstock for many common products, including concrete, glass, detergents, and toothpaste. Sodium silicate is classified as a non-hazardous solid waste under the Resource Conservation and Recovery Act (RCRA) and can be readily recycled or disposed of in municipal waste streams.

To make this an entirely clean energy alternative, SiGNa is developing a recycling system for both sodium silicate and the fuel cartridges, which are made from an impact extruded aluminum can that can be recycled in any typical recycling collection. Initially, SiGNa will establish a mail-based recycling program, whereby users mail empty fuel cartridges to SiGNa and full cartridges

1 Limited Streamlined Life Cycle Assessment of Sodium Silicide for Use in Fuel Cell Batteries, December 2010. Report available on request.

will be returned. The sodium silicate in the cartridges will be amassed and provided as a feedstock to other industries and the cartridges will be recycled. Over time, SiGNa will establish a localized canister recycling program, similar to the Blue Rhino propane tank exchange program, where users return empty cartridges to local retail outlets who swap empty fuel cartridges for full cartridges. In this way, neither the sodium silicate nor the cartridges will enter the waste stream and this energy technology will have zero negative impact on the environment.

Reduced Cost of Energy

Environmental benefits have played a key role in the drive to develop hydrogen energy. However, environmental concerns alone will not force market acceptance of hydrogen power. The public continues to demand low cost energy and if hydrogen is to be widely accepted, it must cost the same as or less than fossil fuel or battery power.

Energy generated by NaSi is significantly less expensive than existing portable power technologies (Table 2). A NaSi fuel cell in reasonable production volumes is ten times less expensive than alkaline batteries and six times less expensive than disposable lithium batteries, *including the cost of the fuel cell*. Put another way, in order to buy enough alkaline batteries to charge a cell phone 100 times (800 W-Hr), a consumer will pay about $967. Lithium batteries are a bit cheaper and will cost about $512 for 100 charges. Customers using a NaSi fuel cell to power their electronics will pay only $89 for 100 uses. *Including the cost of the fuel cell, consumers will save nearly $900 by charging their electronics with a sodium silicide fuel cell.*

Table 2. Cost comparison of existing energy technologies.

	Weight			Cost			
	Fixed Weight (kg)	Energy Density (W-hrs/kg)*	Total Wt. (kg) (3000 W-hrs)	Fixed Cost ($)	Variable Cost (3000 W-hrs)	Total Cost (30 Uses)	Notes
Dow-SiGNa Cartridge	3.7	1,333	6	$125	$18.75	$688	$10 /kg NaSi
Gasoline Generator	13.4	440	20.2	$1,000	$10.13	$1,304	$4.50 /gal Gas
Alkaline Batteries		140	21.4		$1,393	$41,786	$65 /140 W-hr battery
Li Rechargeable Batteries		100	30.0	$2,850	$3.00	$2,940	$95 /100 W-hr battery $1 /kW-hr Recharge

* Includes packaging

3. APPLICABILITY AND IMPACTS—MARKET DEVELOPMENT STRATEGY

NaSi-based fuel cells are a disruptive energy solution that can fully replace batteries, small combustion engines, and even gasoline in some automotive markets. Consumers and product manufacturers continue to demand ever-higher energy densities and longer run times. Existing battery technologies simply cannot meet the growing demand for portable power as consumers seek faster connectivity, streamed content and brighter screens. Li-based batteries have advanced in recent years, but internal heating issues and theoretical energy densities limit their further improvements. Small combustion engines are also not a long-term solution. These engines operate at very low efficiencies for applications less than 3kW and emit disproportionately high levels of air pollutants.

NaSi fuel cells are ideal for a wide variety of consumer and industrial applications, ranging from 1 W to 3kW (Figure 3).

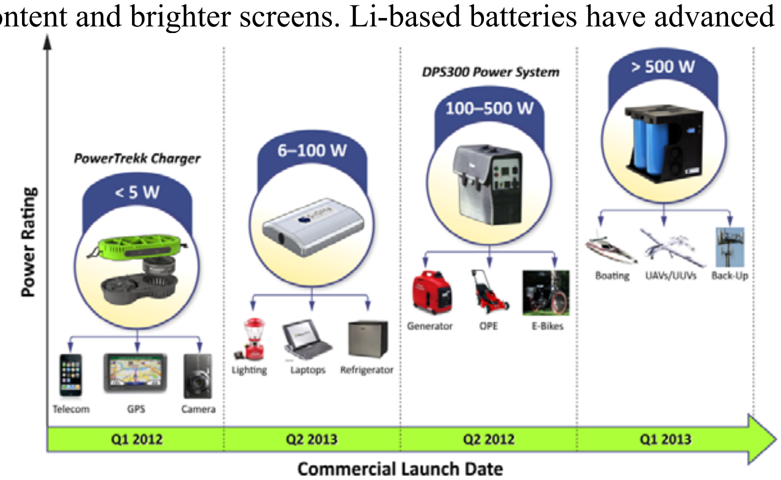

Figure 3. Market segments for NaSi fuel cells.

NaSi powered fuel cells outperform battery and small IC engines, in both performance and cost terms. To scale to the point of mass acceptance, NaSi is first being introduced to several consumer electronics segments (Figure 3). Deployment of fuel cells in these initial markets will help develop a manufacturing and supplier base, increase production volumes to lower fuel cell costs, and broaden public familiarity with fuel cells energy. Growth of hydrogen energy for electronics segments will also be essential to achieve the economies of scale and price decreases needed to bring the price of hydrogen energy in line with fossil fuels. This market development approach will prepare for and subsidize entry into longer-term markets, like back-up power and general transportation uses.

Consumer Electronics (Near-Term Market)

There are 307 million smartphones, eReaders, notebooks and laptops in use today. Consumers continue to demand higher-density power supplies to power faster data networks and power-hungry applications, like video streaming. Li-ion batteries have reached their practical energy limits and will not be a long-term solution for the consumer electronics markets. NaSi fuel cells, however, have a much higher energy density, almost 10 times greater than batteries (Figure 4) and provide a significant increase in power availability and lifetime.

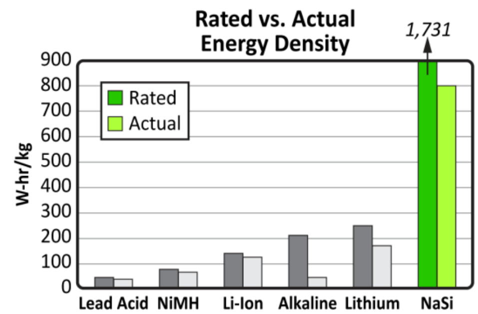

Figure 4. Energy comparison.

NaSi is being introduced globally in various electronics products. SiGNa has licensing agreements in place with manufacturers (in Europe, Asia, and North America) that are launching products powered by NaSi and NaSi/$NaBH_4$ fuel cartridges. These products are a logical starting point to catalyze more familiarity with and use of hydrogen as an everyday energy source. The first product introduced to the consumer market is the PowerTrekk™ (Figure 5), a fuel cell charger that can power any low power device using a USB port, including mobile phones, cameras, and GPS devices. PowerTrekk™ is available now in Europe; beginning in April 2012, a leading U.S. sporting goods retailer will distribute the PowerTrekk™ and PowerPukk™ cartridges at 120 outlets.

Figure 5. PowerTrekk recharger, ***the world's first IEC approved complete hydrogen fuel cell system.***

Nonroad Engines and Power Equipment (Mid-Term Market)

Gas-powered lawnmowers and other gas-powered outdoor power equipment continue to be a major source of pollution in the U.S. The EPA estimates that 14% of GHG emissions come from small spark ignition engines, with 5% coming from lawnmowers alone (one gas-powered lawnmower emits 11 times the air pollution emitted by a new car for each hour of operation). A recently announced guideline (EPA 420-F-08-013) requires an emission reduction from these engines of 630,000 tons of HC, 98,000 tons of NOx, 6,300 tons of particulate matter, and 2.7 million tons of CO. SiGNa is working with a leading power equipment/lawnmower distributor to develop a hydrogen lawnmower to replace their gas mower. By replacing these engines with NaSi fuel cells, up to 14% of the GHG emissions in the U.S. can be completely eliminated.

Distributed and Back Up Power (Near-Term Market)

There are many places in the world where electric grids do not exist and power for daily, backup (for emergency outages) and standby (for frequent outages due to an unreliable grid) uses is critical. SiGNa is developing a NaSi fuel cell generator that provides a reliable and portable source of electricity for computers, refrigerators, water pumps, medical and telecomm equipment. This generator (Figure 6) is being developed through a grant with the U.S. Agency for International Development (USAID) as a way to bring power to impoverished areas. The DPS300 will enter field testing in early 2012 and SiGNa is working with U.S. agencies, world governments, and major OEMs to deploy the generator to needy communities. Similarly, the NaSi fuel cells can fully replace battery backup power. As more countries mandate eight-hours of backup operating time for telecomm and emergency communications services, this market is growing well and is targeted to exceed $975 million in 2014.

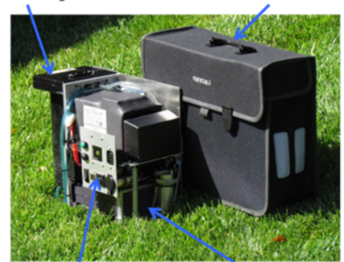

Figure 6. DPS300 generator.

General Transportation (Long-Term Market)

The transportation sector presents the biggest market and most potential for environmental benefits. NaSi is scalable for transportation uses, but using fuel cells for transportation applications presents a greater technical challenge and will lag behind other fuel cell segments. Unfortunately, the auto industry attempted to replace the combustion engine directly with fuel cells at the on-set of the fuel cell industry. This approach was simply not technically feasible. As a comparison for the semiconductor industry, this would have been like trying to build a Pentium chip in the 1950s when the transistor was first invented.

SiGNa is working to introduce NaSi fuel cells to the auto market in the near-term. Currently, most electric vehicles (EVs) are complemented with a combustion engine and gas tank to extend the travel range and power electronics, radio, and air-conditioning. SiGNa is working with several automobile companies to replace the combustion engine and gas tank in their EVs with a smaller, range-extending NaSi fuel cell. NaSi cartridges can be immediately sold at gas stations and convenience stores, eliminating the need to build a hydrogen infrastructure. This intermediate step will pave the way to consumer familiarity and acceptance of fuel cells and take an evolutionary step toward their full integration into automobiles as a hybridized system.

4. HUMAN HEALTH AND ENVIRONMENTAL BENEFITS

By replacing lithium batteries and internal combustion engines with NaSi-based fuel cells, the U.S. will significantly reduce the amount of greenhouse gases being released into the atmosphere and toxic materials entering the waste stream.

Reduction of Harmful Emissions and Pollutants

The environmental benefits from this technology will be realized as NaSi fuel cells replace inefficient batteries and gasoline generators, which together dominate the portable power market. Gas generators and other small (<3 kW) combustion engines are responsible for 14% of the total manmade Volatile Organic Carbon (VOC) emissions in the U.S. today. In addition, dry cell batteries create more than 3,267 tonnes of waste each year in the U.S., with an equivalent CO_2 emission of 14,048 tonnes /year. By replacing disposable batteries and small combustion engines with NaSi fuel cells, greenhouse gas emissions in the U.S. will immediately be reduced by hundreds of tonnes. Additionally, the solid waste associated with batteries can be eliminated entirely as NaSi's only by-product is a feedstock for several other consumer goods and industrial processes. With this technology, the U.S. will not only reduce its dependence on Li-batteries, which are produced offshore, but dramatically reduce greenhouse gases and toxic materials.

Reduction of Toxic Waste, Lead and Mercury

Replacing batteries and small IC engines will significantly reduce the toxic waste entering the waste stream. Disposable batteries are a significant environmental hazard, particularly when distributing large amounts of energy. More than 3 billion batteries (125,000 tons of regular and rechargeable batteries) are thrown away in the U.S. each year, enough to circle the earth six times if laid end to end or to fill 600 large yellow school buses.[2] Even assuming that only 20% of the battery market switched to hydrogen fuel cells, the adoption of NaSi fuel cells represents a profound reduction of more than 500 million batteries annually.

[2] RCRB & National Geographic: http://www.panasonic.com/environmental/rbrc_lesson_plan.pdf.