

Lessons Learned- Lithium Silicide Hydration Fire

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Keywords

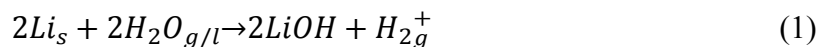
Lithium silicide, fire, lessons learned, water-reactive

Abstract

Alkali metals, such as lithium, sodium, potassium, etc., are highly reactive elements. While researchers generally handle these metals with caution, less caution is taken when these elements have been “reacted”. Here, a recent incident is examined in which a pair of researchers ignited a lithium silicide alloy sample that was assumed to be fully hydrated to lithium hydroxide and, thereby, no longer water-reactive. However, variations in the original chemical composition of the lithium compounds examined resulted in select mixtures failing to hydrate and react completely to lithium hydroxide in the timeframe allowed. This gave rise to residual unreacted, water-sensitive lithium silicide which resulted in a violent exothermic reaction with water and autoignition of the produced hydrogen gas. This Letter describes this incident and improvements that can be implemented to prevent similar incidents from occurring.

Water-Reactive Lithium Silicide Dangers

Alkali metals (lithium, sodium, potassium, etc.) and their alloys are among the most reactive metals,¹ many reacting with atmospheric gases, water, and organic materials.² This is largely due to their low ionization energies and the large atomic radii of the alkali metal,³ which allows their electrons to be easily donated making them strong reducers.⁴ Lithium and lithium alloys therefore can vigorously react with water to produce lithium hydroxide (LiOH) and hydrogen gas (example of the pure lithium metal reaction with water, reaction 1),



the former being caustic and the latter being extremely flammable.¹ One example of a lithium alloy which reacts with water in a similar fashion is lithium silicide (Li_xSi_y), examined in this Letter. Lithium silicide is a complicated alloy but generally the various phases are more stable than pure lithium metal.⁵ However, lithium silicide is pyrophoric like lithium metal, with its reaction with water being extremely exothermic,⁵⁻⁶ autoigniting the hydrogen gas produced when the temperature reaches $585\text{ }^\circ\text{C}$,⁷ or, in some cases, the metal alloy itself (the temperature at which this occurs varies depending on environment),⁸ resulting in an explosion and subsequent fire (example lithium silicide ignition, Figure 1).

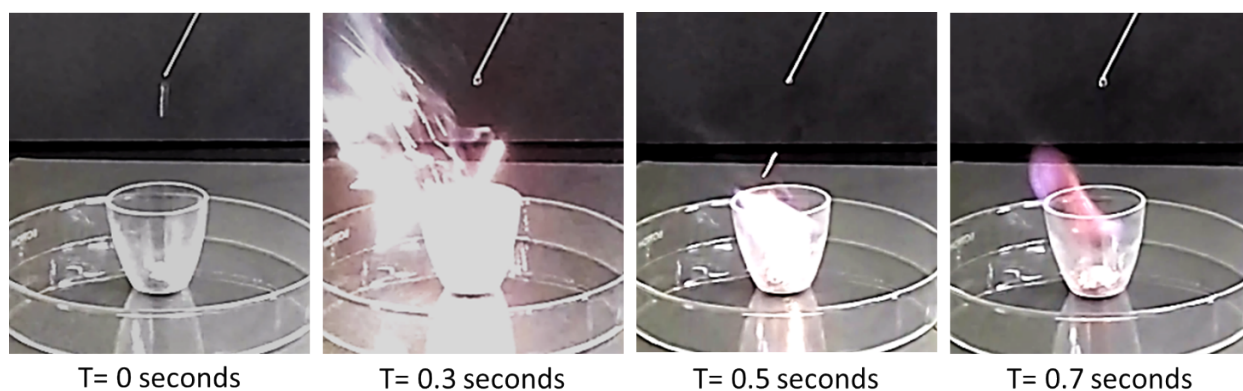


Figure 1: Flame resulting from lithium silicide (<0.1 g) reaction with water.

What Happened?

A pair of researchers were performing an acid digestion on a set of water-sensitive lithium silicide-electrolyte (lithium bromide, LiBr; potassium bromide, KBr; and lithium chloride, LiCl) mixtures (~3.0 grams per sample) in 100 mL polypropylene tubes. These samples were slowly hydrated in a ~90% relative humidity environment for one week prior to digestion to produce a safe, non-water-sensitive lithium hydroxide compound. One researcher began slowly adding 5 mL of water into the first hydrated sample mixture, rotating the tube to ensure even wetting of the material. With no reaction, an additional 10 mL of water was added more quickly, followed by multiple acid

digestion steps with no issues. However, when adding water to the second sample, in the same manner, a fire quickly ignited. With the addition of only 250 uL of water, a bright pink flame extended out of the top of the vessel 4-6 inches. With ten additional sealed vessels of the same sample type in the tube rack which could catch on fire, the researcher decided to quickly transfer the rack to a nearby sink where the fire could be extinguished via water saturation into a secondary container (empty plastic bucket). Fortunately, no other tubes ignited and, while the inflamed tube did melt under the temperature, the secondary container caught and contained the material (Figure 2). Following the extinguishing of the fire, the researchers cleared the lab to minimize exposure to the light fumes.



Figure 2: Post-accident photo of the tube containing lithium silicide fire.

What Was The Cause?

The slow hydration of water-sensitive alkali metals is a procedure very familiar to the involved researchers and laboratory, with a standard operating procedure (SOP) developed specifically for the safe hydration of these materials. In short, samples are weighed into glass or plastic vials with ample space for expansion of the sample volume. These samples are placed into a humidity

chamber set at 90% relative humidity. Samples are removed, mixed, and weighed every 24 hours prior to returning them to the humidity chamber. Utilizing this hydration method, multiple previous small-scale hydration experiments, 0.1-0.15 g (Figure 3A) and 1.0 g (not shown), were observed to reach a terminal metal hydroxide formation point, indicated by a plateau in the weight gain, within seven days. Furthermore, randomly selected samples from the large scale, 3.0 g set were weighed throughout the hydration to observe the terminal metal hydroxide point of 3.0 g samples. With these preliminary studies and preventative actions taken, the researchers investigated possible factors which led to the accident.

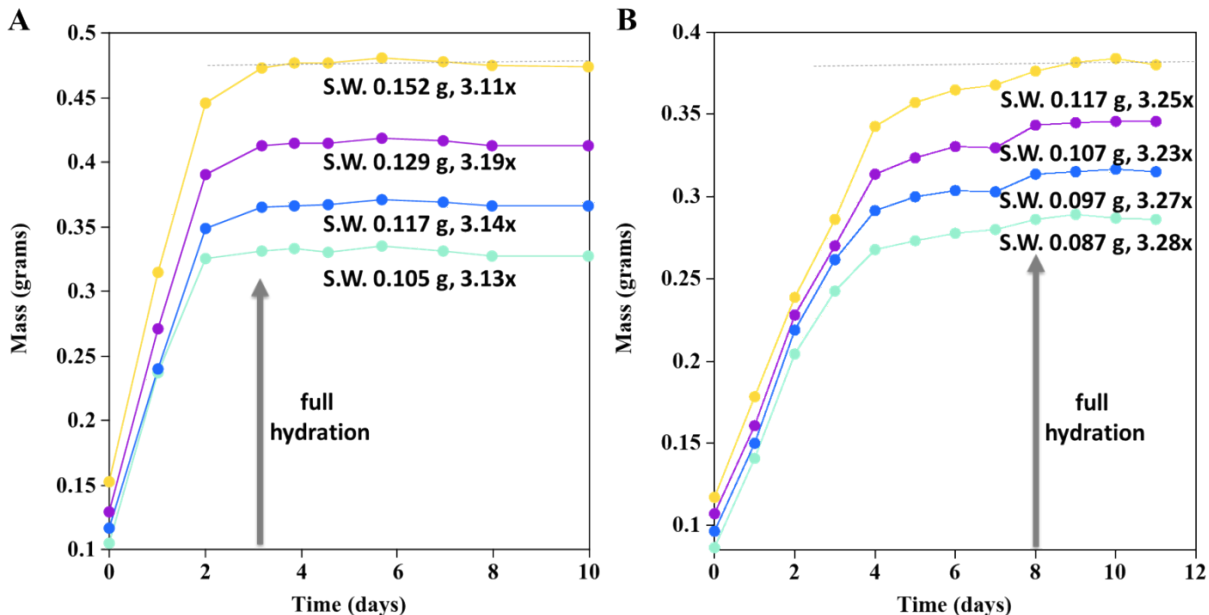


Figure 3: Plots of mass changes during hydration of LiSi-electrolyte mixtures (A) and pure LiSi (B). Starting weights (S.W.) and total weight gain are indicated for each replicate. The terminal metal hydroxide formation point is indicated by the plateau in weight (dashed line), while the initial point of full hydration is also indicated (arrow).

Due to the damage to the sample caused by the fire and extinguishing, a post-mortem analysis of the sample was not possible. However, replicates of the samples which had not yet gone through the water addition, plus knowledge of the chemical compositions, both led to one conclusion:

Select samples were not fully hydrated. Additional small-scale hydration experiments using pure LiSi showed much slower hydration, *i.e.*, a longer hydration time to reach the “full hydration” point (Figure 3B), compared to LiSi-electrolyte mixtures (Figure 3A). The more hygroscopic electrolyte salts may accelerate the hydration of the LiSi particles, thereby decreasing the time to full hydration. Pre- and post- hydration images illustrate the visible change in the conversion of LiSi (Figure 4A) to LiOH (Figure 4B). A laboratory investigation revealed multiple ways full hydration was not completed, including the following:

- While randomly selected samples were weighed to observe the terminal metal hydroxide formation point, all samples should have been weighed to ensure consistent hydration throughout all the samples.
- Inconsistent mixing during the hydration process caused a small hardened crust to form on the top of select samples which was observed in some replicates. This slowed the conversion of lithium silicide (water-sensitive) to lithium hydroxide (not water-sensitive) of the material below that 'crust'.
- The most significant influence was the composition of the samples themselves. In an attempt to be unbiased, the samples were provided as part of a blind study. The researchers believed all the material provided consisted of a mixture of LiSi, LiBr, KBr, and LiCl, which has been handled by the researchers many times. However, it was theorized select samples were taken prior to the addition of the electrolyte salts and consisted only of LiSi. Since lithium salts (LiBr and LiCl) are some of the most hygroscopic salts known (high water absorption capacity), it was not surprising that a pure LiSi alloy would hydrate at a slower rate compared to the LiSi-lithium salt mixtures. This is due to moisture diffusion in the dispersed phase, *i.e.*, the LiSi-electrolyte powder phase. Since the lithium salts hydrate at a faster rate than the LiSi alloy,

these salts can facilitate faster hydration of the LiSi through moisture diffusion, *i.e.*, the LiSi in LiSi-electrolyte mixtures is hydrated both from the high moisture atmosphere as well as through moisture diffusion from the lithium salts. This theory was confirmed through conversations with the study coordinator who didn't realize the change in composition would change the handling of the material. Unfortunately, the randomly selected samples which were weighed throughout the hydration were LiSi-electrolyte mixtures.

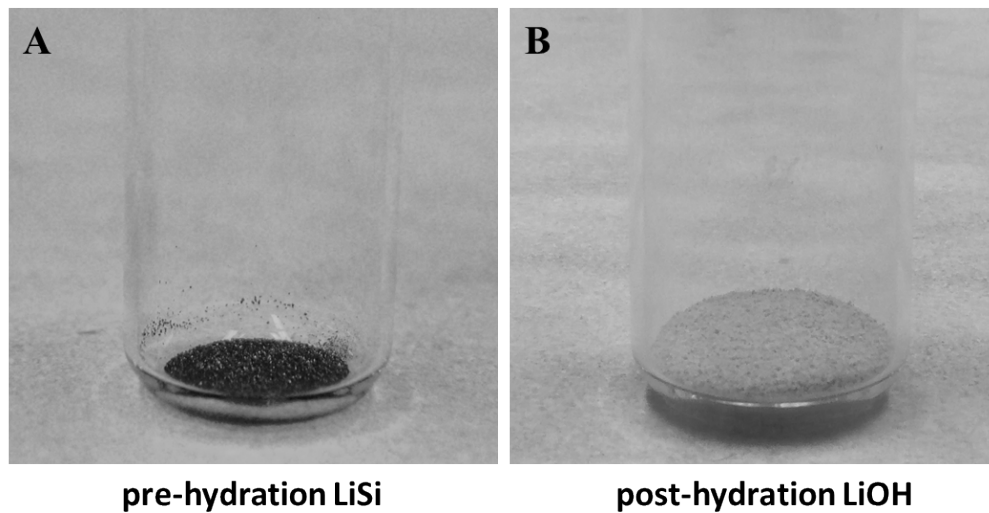


Figure 4: Images of lithium silicide powder (A) and post-hydration lithium hydroxide (B).

What Corrections Were Made To Laboratory Procedure?

The remaining samples in this particular incident were placed back into the hydration chamber and allowed to fully hydrate while the researchers' investigation concluded. Following the investigation, several improvements to laboratory procedure were determined, with the hydration SOP adapted to include the following:

- During the hydration process, LiSi and electrolyte samples are mixed daily to ensure non-hydrated material has access to humid air. This includes the use of a stir bar/plate for mixing during hydration in the humidity chamber, preventing the hardened crust from forming.

- Throughout the hydration process, all samples (not just a representative sample set) are weighed to correctly assess the completion of hydration based on differential weight gain.
- The subsequent addition of water to hydrated samples is completed in a secondary container filled with an ice bath to keep exothermic reaction temperatures low.
- Samples are hydrated in or transferred to a glass container prior to water addition. Glass containers are capable of withstanding the short burst of heat produced from the short lifetime of a LiSi fire (assuming < 3.0 g of LiSi).

How Can Incidences Like This Be Prevented?

An evaluation of the risks related to water-sensitive compounds revealed particular actions which can prevent incidences like the presented accident from occurring, including:

- Ensure there is a full and clear understanding of the chemicals used in each experiment (*i.e.*, if the experiment is part of a blind study, ensure all components present in the samples have been disclosed).
- Thoroughly develop an SOP for the use of alkali metals, consulting the safety data sheet for hazard analysis of all components of the experiment and listing proper materials (*i.e.*, containers and secondary containers capable of withstanding the heat generated from an alkali ignition), protection, and procedures.
- Provide all personnel working with alkali metals with the proper training and personal protective equipment (PPE), ensuring they have reviewed the SOP prior to the experiment.
- When possible, experiments involving alkali metals should be carried out in a glove box. If a glove box is impractical for the experiment at hand the experiment should be carried out on a

small scale (< 2.0 g) in a fume hood free of incompatible materials; acids, moisture, oxidizing agents, and flammable materials.

- Ensure a Class D fire extinguisher is available before beginning experiments with alkali metals.
- If working with larger quantities for the first time, we recommend scaling up in small increments, as increasing quantities may require significant method alterations.
- Lastly, if slow hydration is needed to convert the alkali metal to an alkali hydroxide, all samples must be weighed periodically to ensure terminal metal hydroxide formation point has been reached for each sample.

Quick Action Tips and Exposure Emergency Protocol

In the event an alkali metal fire does occur, properly trained personnel and a response plan are essential. As with any fire, do not attempt to extinguish if in doing so you will put yourself at risk. If fighting the fire is not a safe option, close the hood sash and back away to safety. Pull the fire alarm to evacuate the laboratory.

If, however, you must extinguish the fire, here are some tips for safely fighting an alkali metal, or specifically lithium silicide, fire:

- Small fires can be immediately smothered using dry dolomite, sand, or, in the case of a lithium fire, Lith-X.⁹
- If none of the above are available and it is safe to do so, a lid may be placed over the reaction vessel to restrict the ingress of oxygen and extinguish the flames. Do not completely seal the container to prevent pressure build-up.

- Larger or uncontrolled fires should be extinguished with a dry chemical fire extinguisher rated for Class D fires. Do NOT use a water fire extinguisher. Fire extinguishers of other types (e.g. CO₂) may blow the powder away, potentially spreading the flames.
- Allow the container and material to cool completely, as it will have likely reached very high temperatures during this reaction. Once cool, collect all the material and dispose of it as hazardous waste. Keep away from water.

In case of exposure, remove contaminated clothing and brush off any remaining material from the skin before flushing with water and washing with soap. For exposure to the eyes, flush the eyes thoroughly with flowing water for at least 15 minutes. In case of inhalation exposure, move to fresh air. Seek medical attention as necessary.⁹

Author Contributions

The manuscript was written through the contributions of all authors.

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Abbreviations

LiSi, lithium silicide; LiBr, lithium bromide; KBr, potassium bromide; LiCl, lithium chloride;

PPE, personal protective equipment; SOP, standard operating procedure

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Graphic Abstract

