

*Materials Innovations in an Emerging Hydrogen Economy*  
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# Hydrogen Production

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## RECENT RESULTS ON SPLITTING WATER WITH ALUMINUM ALLOYS

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### ABSTRACT

Recently, we reported that solid alloys containing Al compositions included 28 wt%, 50 wt%, and 80 wt% Al when placed in contact with water at or near room temperature would react to generate hydrogen gas, heat, and alumina. The hydrogen mass yield of the reaction was 100%. The Ga was found to be completely inert, recoverable, and hence recyclable. The Ga can be of low purity and when coupled with a current electrolysis efficiency of reducing alumina to Al of 50% makes this an economically viable process for creating hydrogen on demand. In this presentation we will discuss the results of some recent experiments to further elucidate the properties of the Al-Ga-water process. We have measured reaction rates of water with the alloys versus reaction temperature, pH of the solution, etc. We have investigated using other solvents including Ga-In, and Ga-In-Sn mixtures. The results of these experiments will be reported at the conference.

### INTRODUCTION

Energy density, safety, and cost are the major factors in determining the delivery of portable, off-the-grid power. This paper explores a means of safe, inexpensive energy storage at an energy density significantly better than that of modern batteries. The methodology analyzed is the depassivation of aluminum which allows aluminum to reduce the oxygen from water. The resultant hydrogen gas can be combusted in an engine or utilized in a hydrogen fuel cell. Moreover, the byproducts of this methodology are simply alumina, water, and heat. This energy storage technology boasts energy density much better than that of batteries, byproducts much safer than those of hydrocarbons, and a cost comparable to gasoline.

### DISCOVERY OF ALUMINUM-GALLIUM-WATER REACTION

In the late 1960's, Jerry Woodall discovered how to split water into hydrogen, alumina, and heat near room temperature using a gallium (Ga) rich aluminum-gallium (Al-Ga) liquid alloy. This discovery was the result of an unexpected event that occurred during his pioneering research on the liquid phase epitaxial (LPE) deposition of Aluminum-Gallium-Arsenide (AlGaAs) layers on Gallium-Arsenide (GaAs) substrates<sup>1</sup>. In the LPE method for AlGaAs, a Ga rich mixture of Al, GaAs and a dopant are prepared in a fixture composed of carbon, high purity alumina, or pyrolitic BN. This mixture is then liquefied by heating the ensemble to a temperature between 600 and 900°C in the presence of an inert gas. After equilibration a GaAs substrate is brought into contact with the melt. The ensemble is slowly cooled over a temperature range of 10 and 50°C. This causes deposition of an AlGaAs epitaxial layer onto the GaAs substrate.

This process is analogous to depositing sugar crystals on strings or sticks by cooling a solution of hot water saturated with sugar. In the LPE process, after cooling a prescribed amount the substrate plus the AlGaAs layer is separated from the melt and the ensemble is returned to room temperature and disassembled. The water splitting effect was discovered when the fixture was rinsed with warm deionized water. The moment the water came into contact with the residual Ga-Al liquid, there was an evolution of hydrogen gas plus a heating of the fixture.

## Recent Results on Splitting Water with Aluminum Alloys

This event was the birth of splitting water with Al-Ga alloys. The technical details of this reaction can be found in US Patent # 4,358,291 issued on Nov. 9, 1982 with co-inventors Jerome Cuomo and Jerry M. Woodall, who were both employed at IBM when the patent was issued. An intriguing and commercially interesting aspect of this invention was the fact the Ga component of the alloy is inert in the process. Even so, since the patented process is about Ga rich Ga-Al liquid alloys, and owing to the high cost of Ga (currently \$350/kg) there was no widespread commercial interest when the patent was issued.

### MECHANISM OF REACTION

Since that time much has happened to improve both the scientific understanding of, and commercial interest in, this process. The basics of how liquid Ga-Al alloys split water are now understood. The liquid Ga-Al alloy has two properties that work together to split water. First, Al itself has enough thermodynamic energy to split water. The oxidation of Al to alumina,  $2\text{Al} + 3/2\text{O}_2 \rightarrow \text{Al}_2\text{O}_3$ , has a very large negative value for the free energy of oxide formation and is a much larger negative number than for the free energy of the oxidation of hydrogen to form water,  $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ . Therefore, Al is able to split water. However, pure Al does not readily split water, due to its passivating oxide (alumina) surface layer that protects it from both rapid oxidation and splitting water. Thus, as a result of this passivating oxide, Al metal is a robust, non corrosive, lightweight metal used for many applications from liquid containers to light weight car frames and engines. Also, except for discarded material, Al metal, unlike gold, does not exist in nature. This is because over many millennia, pure Al oxidizes in air to form alumina. Thus, when Al metal is made, it starts the process as alumina, a component in an ore known as bauxite. Refining alumina is discussed further in the document.

Upon dissolving Al into liquid Ga, the alumina layer that instantly forms from exposure to air or water at the surface is either discontinuous or porous. In either case the surface of the Ga-Al liquid is not passivated. As a result, when water contacts the surface of the liquid, Al atoms at the surface split the water, liberating hydrogen and heat with the formation of alumina. Since the liquid is fluid, the alumina cannot form a bonded layer at the liquid surface that would passivate pure, solid Al. Instead, the alumina is swept away by convection or agitation as a suspension of alumina particles in the water. The surface of the liquid alloy is now depleted of Al. This depleted region at the surface is replenished via diffusion or convection of Al from the bulk to the surface where it continues to split water. This process continues until all of the Al in the liquid alloy is converted to alumina. To summarize, liquid Al-Ga alloys rich in Ga split water because the Al component is not passivated as it is in solid pure Al.

Next is the question of why the Ga is inert in the process. Unlike Al, the free energy of the oxidation of Ga to make gallium oxide is a much smaller negative number than the value for Al. In fact it is smaller than the negative number for the oxidation of hydrogen to water. This means that even though Ga will oxidize in air, it cannot split water. Hence, when Al-Ga liquid alloys split water the Ga component is inert. It will not even oxidize in water that is free of dissolved oxygen. This fact makes the Ga-Al alloys technologically very attractive for making hydrogen on demand, since the low cost Al does the splitting while the Ga is inert. This means that the Ga is totally recoverable. Since it can be recycled indefinitely, it can be treated as a capital cost, rather than a materials expense in a commercial enterprise. However, from a commercial vantage point, using Ga rich Al-Ga liquid alloys would never be considered as a cost competitive method for making hydrogen gas. The Al-Ga + water reaction still boasts a safe material for energy storage and transport that can deliver hydrogen on demand, and can be recycled back to the initial condition by currently used and widely known industrial processes.

### MATERIAL PURITY

With the world's growing interest in alternative, Woodall decided to investigate three questions concerning water splitting using liquid Al-Ga alloys. First, the purity of the alumina reaction product was investigated. Second, the recovered Ga was investigated. Third, the possibility of excess Al in contact with liquid Ga continually dissolving in the presence of water was investigated. The results of studies were, 1) except for traces of Ga, the alumina had a purity of 99.999, i.e. 5-9s when 4-9s Ga and 4-9s Al were the starting materials; 2) when the traces Ga were separated by centrifuge, 99.99% of the Ga could be recovered; 3) Al would not continuously dissolve into Al depleted liquid Ga in the presence of water. This last result was somewhat discouraging from a technology commercialization point of view. Had it worked, one could envision a system with a small amount of Ga being operated such that Al could be intermittently feed into the Ga and reacted with water to produce hydrogen on demand. However, this did not happen and the reason is not understood. On the positive side, the 5-9s alumina has economic value as a passivating agent for Si chips.

### ALLOY RATIOS

In 2005, a continuation of the work on splitting water with Al-Ga alloys began at Purdue University. By late summer, investigation was under way making alloys richer in Al. The first of such investigations was forming a liquid alloy with a composition of 28 wt% Al, 72 wt% Ga (GaAl<sub>28</sub>). This was done in an elementary way by placing the elemental components into a stainless steel cup and heating it on a hot plate with a cover that allowed the hot melt to be purged with nitrogen gas. The temperature of the hot plate was set to about 400°C to form a liquid GaAl<sub>28</sub> alloy. The hot plate was then cooled to room temperature. Our expectations were that the resulting material would be in a slush-like state, with crystals of Ga-saturated-solid-Al in a matrix of liquid Ga. What happened instead was the formation of a meta-stable solid. To great surprise and joy, a piece of this solid alloy was chipped off and placed it in a beaker of water. It reacted, i.e., it split the water into hydrogen, heat, and alumina plus liquid Ga. This was the first breakthrough in making solid Al-Ga alloys split water.

Over the next year and a half, much time was spent investigating the water spitting properties of the GaAl<sub>28</sub> alloy. Most experiments were devoted to making enough material to react in a small propane tank to produce hydrogen and then use this hydrogen to demonstrate a GENSET. It was also shown that all of the Al in the alloy reacted to make hydrogen gas in the tank experiments. In the Spring of 2006 we began investigations of solid Al alloys with even higher Al compositions, including an alloy of 80 wt% Al, 20 wt% Ga, (AlGa<sub>8020</sub>), and an alloy of 50 wt% Ga, 50 wt% Al (AlGa<sub>5050</sub>). The results of these investigations were incorporated into a conversion patent of the provisional patent filed in May of 2007, and presented at the 2nd Energy Nanotechnology International Conference, Sept. 5-7 2007, Santa Clara, CA., and published in the Proceedings of this conference<sup>2</sup>.

Also, during the summer and early Fall of 2007, the research group found that by substituting an alloy of Ga-In-Sn with a eutectic melting point near 10.7°C<sup>3</sup> for pure Ga, in the 8020 and 5050 alloys, the water splitting reaction could initiate and sustain itself at low temperatures. This opened the possibility of employing this technology in cold weather environments and applications. Also, the 5050 technology was exported to an external vendor to test the validity of using standard industrial processes in the creation of the innovative aluminum alloys. Early tests of these samples validate the internal sample results: the vendor sample splits water.

## Recent Results on Splitting Water with Aluminum Alloys

This is all prolog material to the implications of a recent and preliminary experiment recently conducted at Purdue. Using a vacuum e-beam melting technique a solid Al-Ga-In-Sn alloy with a composition of 95 wt% Al and 5 wt% Ga-In-Sn (95-5) was fabricated. This turns out to be a major breakthrough technologically and economically.

First, this alloy does not react directly with water. However, bringing this solid alloy into contact with a melt of Ga-In-Sn in the presence of water results in the liberation of hydrogen in the water until either all the aluminum or water is consumed. Second, the Ga-In-Sn component of the 95-5 alloy is so volumetrically small that a simple analysis predicts a cost of energy of \$0.0732 per kWh.

### HIGH ALUMINUM ALLOY PRODUCTION

Since the active part of the alloy is the aluminum, any other components are increasing the processing costs and weight of the alloy. It is of interest to study the properties of high aluminum content alloys (>80% Al). In our laboratory produced alloys, we have faced difficulty in getting a homogeneous sample due to limits in the ability of our smelt oven. The current procedure used is to melt a slug of aluminum in a carbon crucible, apply Ga-In-Sn to the top of the Al, then rebake the apparatus at 750°C for 4 hours.

Previous experiments consisted of aluminum rods as an aluminum source. This approach was revealed to be unacceptable due to the aluminum oxide forming barriers to liquid diffusion. A single slug of aluminum was substituted for the rods to reduce the effect of the aluminum oxide.

### HYDROGEN GAS PURITY

Since the conversion efficiency for fuel cells is higher than that of combustion engines, it is of interest to investigate the viability of using the resultant hydrogen gas in a fuel cell. For use in a fuel cell, high-purity hydrogen gas is required. There are a few forbidden gasses for Proton Exchange Membrane based fuel cells, as listed in Table . This table also lists the state of the current methodology for delivering high-purity hydrogen gas by splitting water with an aluminum alloy. The high level of water is expected. The high level of carbon dioxide and nitrogen are believed to be from gas dissolved in the reaction water.

Table III. SAE J2719 Nov 2005 hydrogen gas specification.

Constituent	Chemical Formula	Limit (ppm)	Current Record
Hydrogen	H <sub>2</sub>	>99.99%	86.99%
Water	H <sub>2</sub> O	5	38000
Total hydrocarbons (C1 basis)		2	200
Helium, Nitrogen, Argon	He, N <sub>2</sub> , Ar	100	98900
Carbon Dioxide	CO <sub>2</sub>	1	200
Carbon monoxide	CO	0.2	U
Total sulfur		0.004	U
Formaldehyde	HCHO	0.01	U
Formic acid	HCOOH	0.2	U
Ammonia	NH <sub>3</sub>	0.1	U
Total halogenates		0.05	N
U=Undetected N=Not tested			

## MICROSCOPY STUDIES

The use of SEM and EDX tools have given some insight to the microstructure of the solid alloys made thus far. Understanding the microstructure of these alloys, we believe, is crucial to understanding how the alloy's reaction with water functions on a microscopic level. In turn, this knowledge could be used to craft alloys with more desirable reaction characteristics. As demonstrated in Figure 1, EDX imaging indicates a noticeable phase separation into Al-rich grains (darker regions) and Ga-In-Sn-rich grain boundaries (brighter regions). Because the mixtures of Ga, In, and Sn used in these alloys are liquid at room temperature, it is believed that these grain boundaries pictured herein are also in a liquid phase. The Al-rich grains, however, remain solid and thus give the alloy its overall solid look and feel.

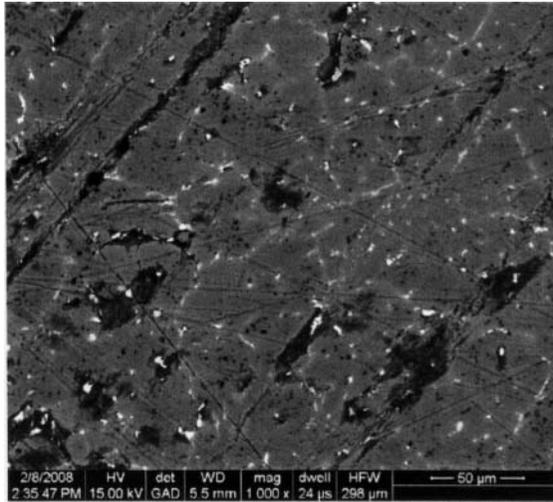


Figure 1. EDX image showing grains and phase separation

These liquid grain boundaries would in theory allow the solid alloys to function microscopically in much the same way that high wt% gallium liquid alloys function macroscopically. Meaning, free Al in the liquid grain boundaries of the material now have a pathway by which to find a reaction site. As Al particles diffuse through the grain boundaries to a reaction site where they react with water to form alumina, the grain boundaries become depleted of Al, which in turn places the grain boundaries in a nonequilibrium condition with the Al-rich grains. In an attempt to restore equilibrium,

Al will leave the grains to enter the grain boundaries, and will also in turn diffuse towards a reaction site, allowing the process to repeat itself until most or all of the Al has been consumed by the reaction. This theory is consistent with the observation that alloys made without In and Sn will not react at room temperatures. Ga without In and Sn remains solid at room temperature, and thus any alloy with solid gallium in its grain boundaries would not be able to provide a pathway to a reaction site for any of the Al the alloy contains.

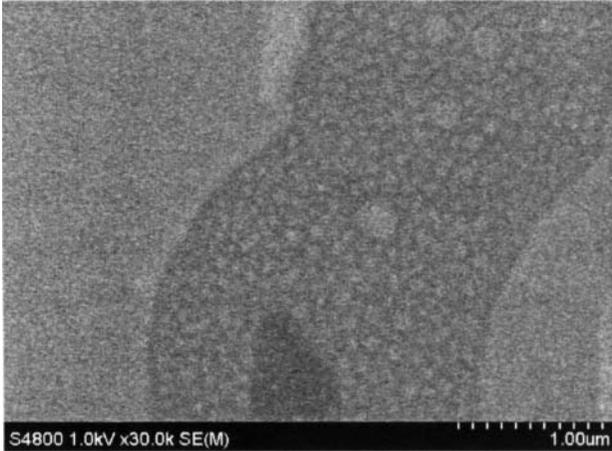


Figure 2. SEM evidence of aluminum nanoparticles in a Ga-In-Sn grain boundary

Figure 2 shows an SEM image illustrating this theory. The image shows what appears to be two Al grains separated by a Ga-In-Sn grain boundary containing Al nanoparticles. As pictured above, these particles average in size between 50 and 100 nanometers.

**CONCLUSIONS**

The addition of In and Sn to these Al-Ga alloys have greatly improved their reaction characteristics. We are now on a path to study the Al-Ga-In-Sn and how fabrication parameters affect the alloys' composition and microstructure. In doing so, we hope to gain a greater understanding of the mechanisms behind the solid alloy-water reaction. Once reaction rate data and hydrogen gas purity have been collected, progress can be made towards incorporating this alloy into systems designed around producing and using hydrogen gas on demand.

**FOOTNOTES**

\*Contaminant limit is the Detection Limit of standard measurement methods. See SAE-J2719 for more details

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