Recent Results on Splitting Water with Al Alloys

Charles R. Allen, Jeffrey T. Ziebarth, Go Choi,
Jerry M. Woodall, Jong-Hyeok Jeon
Purdue University

Overview & History

- Originally discovered by Prof. Jerry Woodall in late 1960's and patented by IBM
- Alloys initially contained low weight percent aluminum (< 5 wt. %) and were reacted in liquid form with water
- New work began on alloys with higher wt.% after Prof. Woodall's arrival at Purdue University in the spring of 2005.
- First successful solid alloy was created in March 2006 and was ~ 18 wt.% Al

Process

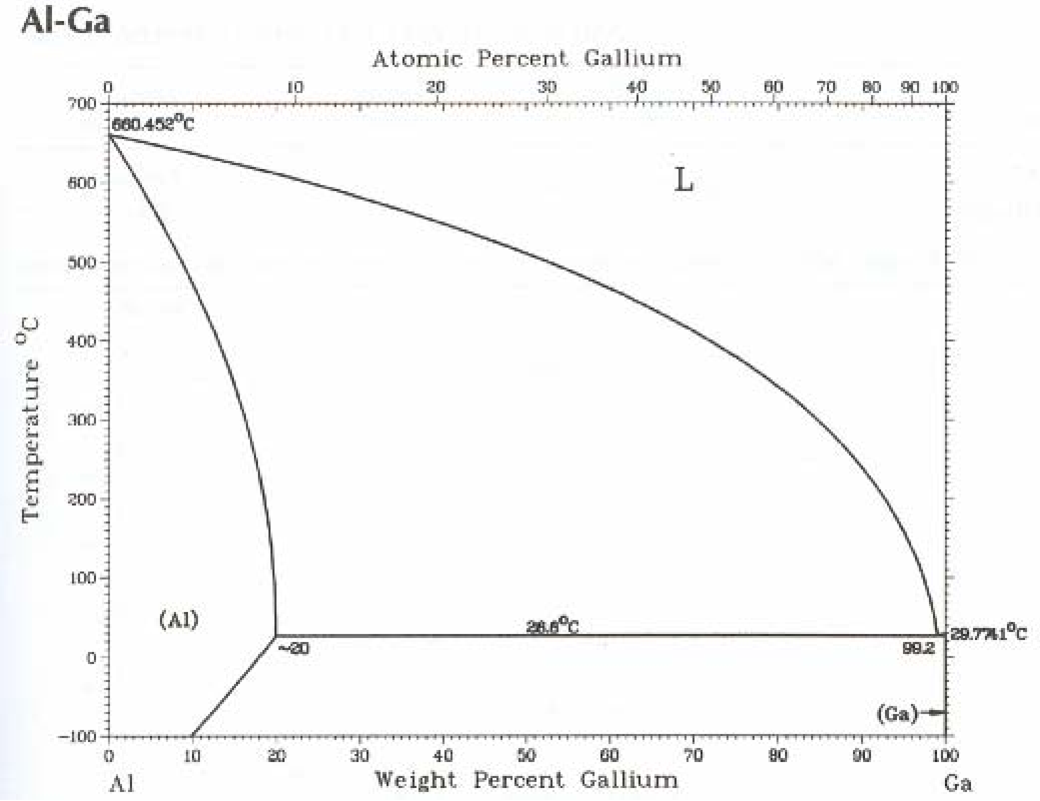
- Aluminum loves oxygen
- Al + H_2O → Al_2O_3 + H_2 + heat
- Al_2O_3 passivates the surface of aluminum to prevent further reaction
- Alloying with gallium prevents this passivation from taking place, and allows all of the aluminum to react

Process

- Gallium allows us to effectively turn aluminum into an energy storage material
- Liquid phase alloys: Al migrates to surface by random thermal motion to contact water and react
- Solid alloys: Mechanisms have yet to be proven through experiment

Fabrication

- Alloys made using either a hotplate or a furnace
- Temperature set according to desired composition by using equilibrium Al-Ga phase diagram
- Inert gas used to prevent oxygen from oxidizing aluminum before it is used in a reaction
- Alloys are then either quenched or allowed to cool slowly



Alloys Created

- 2 wt.% aluminum (original IBM experiment)
- 28 wt.% aluminum (50-50 atomic %)
- 80 wt.% aluminum ("sugar crystal" method)

Alloys Created

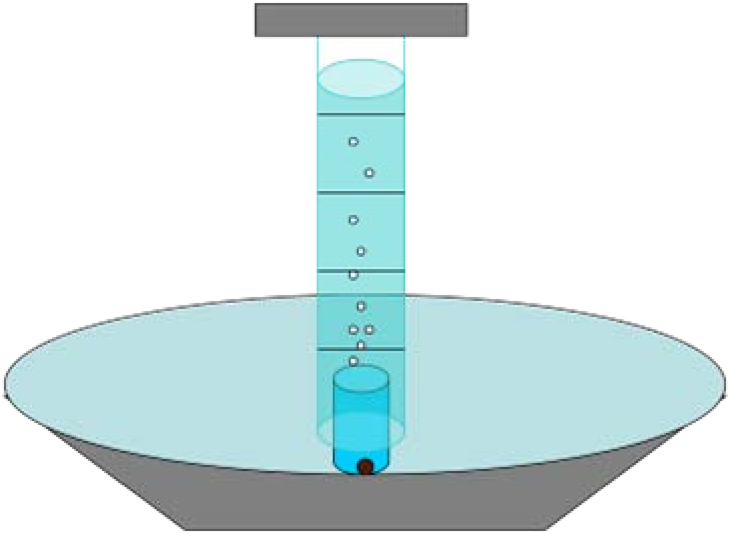
- Aforementioned have gallium as the only alloying agent
- Gallium eutectic with indium and tin to improve alloy characteristics
- Current efforts focus on 50 wt.% aluminum with 50 wt. % Ga-In-Sn and 95 wt.% aluminum with 5 wt.% Ga-In-Sn

Goals

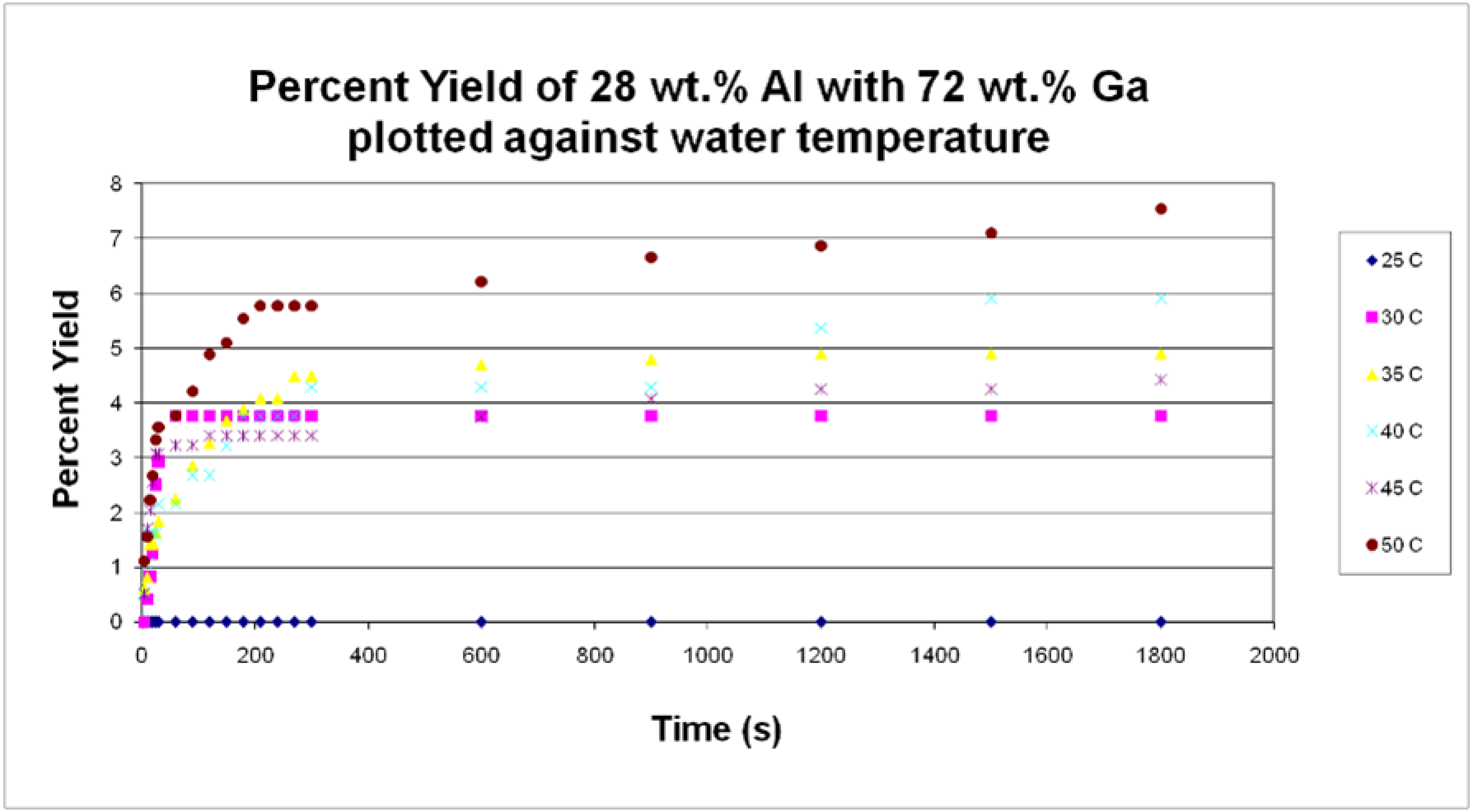
- Obtain reaction rates of alloys for system design
- Hydrogen gas purity measurement (PEM fuel cell requirements are demanding)
- Exploration of the Al-Ga-In-Sn system
- Microstructure analysis of alloys to explain reaction mechanisms (EDX)
- Cooling rates, their effect on microstructure and reaction characteristic

Experimental Setup

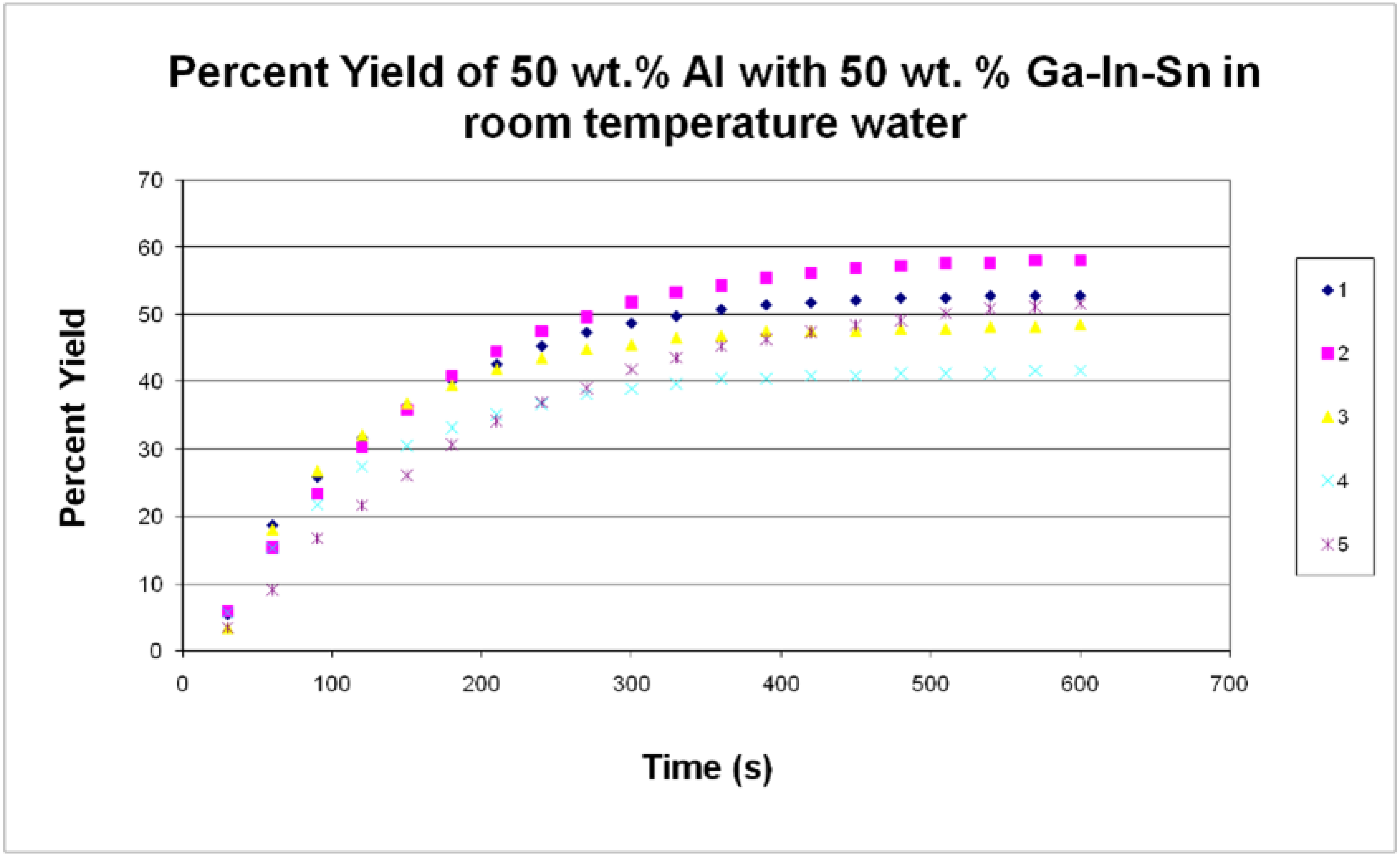
- Inverted graduated cylinder + stopwatch
- Volume of hydrogen produced is recorded as a function of time and compared with theoretical yield
- Theoretical yield is
  (alloy mass)x(wt.% Al)x(1.359 Liters H_2 per gram Al)



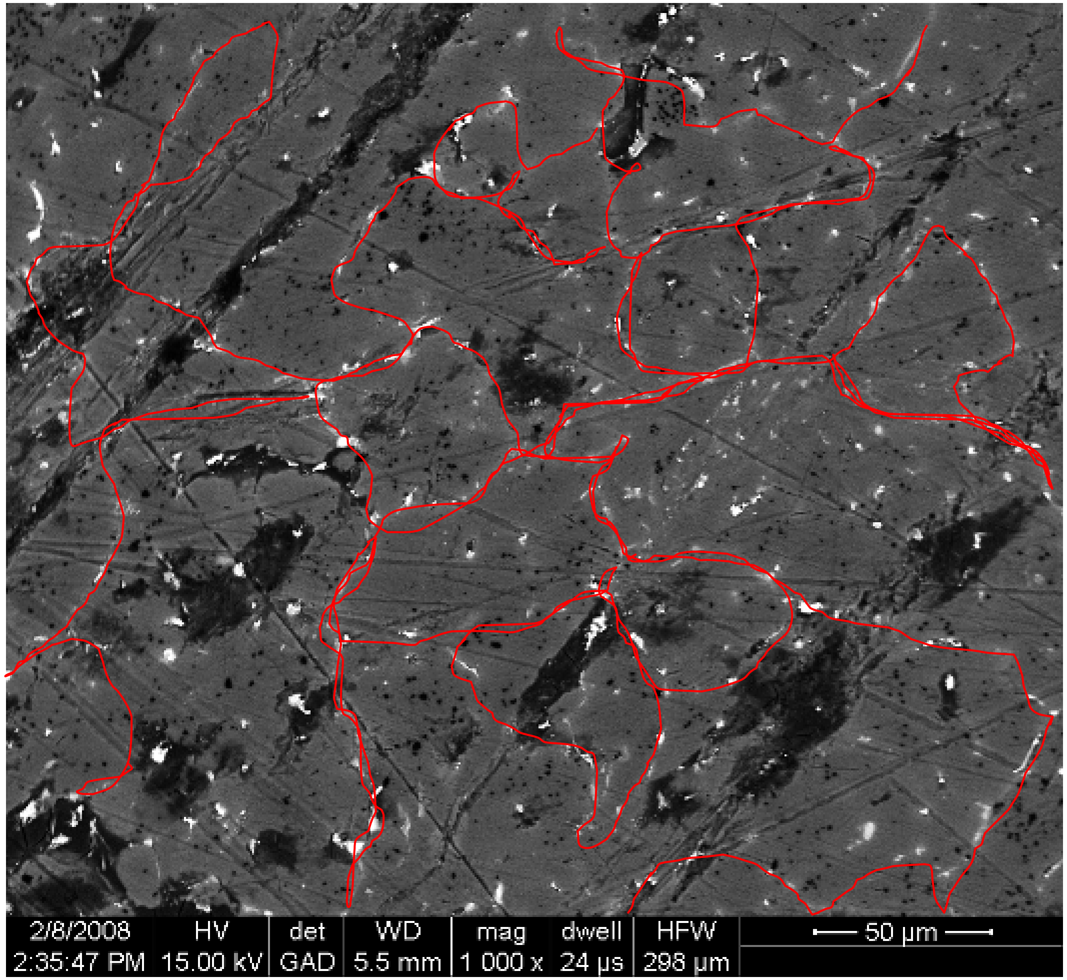
Preliminary Results



Preliminary Results

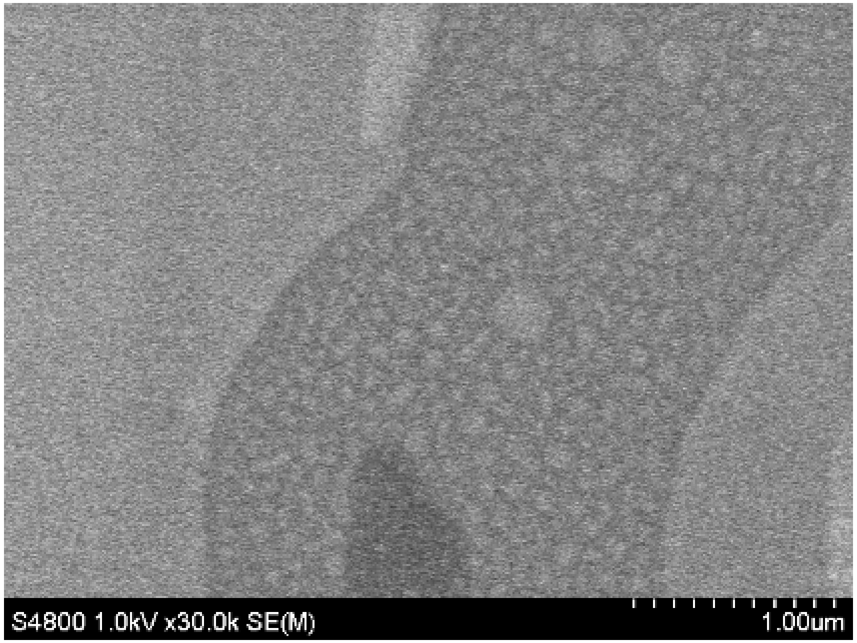


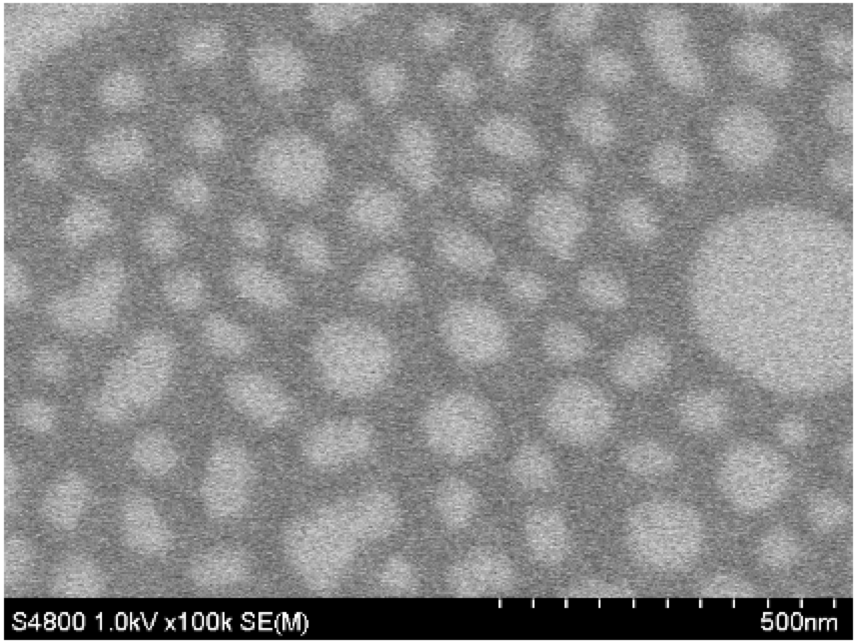
Microscopy



EDX image of 95 wt.% aluminum sample. Brighter regions indicate elements of larger atomic number (Ga, In, Sn). Phase segregation and grain boundaries can be seen.

Microscopy





SEM image of what is believed to be a grain boundary of Ga-In-Sn containing Al nanoparticles

Conclusions

- Ga-In-Sn eutectic greatly improves reaction characteristic over pure gallium
- Liquid phases believed to be an essential part of the reaction mechanism
- Preliminary microscopy work indicates phase separation into Al-rich grains with Ga-rich grain boundaries

Challenges

- Mapping and understanding the Al-Ga-In-Sn system
- Moving towards higher Al content while still maintaining a desirable reaction characteristic (Ga & In are expensive)
- Quenching alloys and quantifying its effect on grain size
- System design

The Future…

- 95 wt.% aluminum presents an economically viable scenario in which nearly pure aluminum is used for the on demand production of hydrogen gas
- Volumetric: 81.3 g/L
- Gravimetric: 5.14 wt.%
- Reaction byproducts are heat and alumina... heat is usable energy, alumina is recyclable
- Expensive gallium and indium are not used in the reaction and hence recoverable

Questions?

http://hydrogen.ecn.purdue.edu

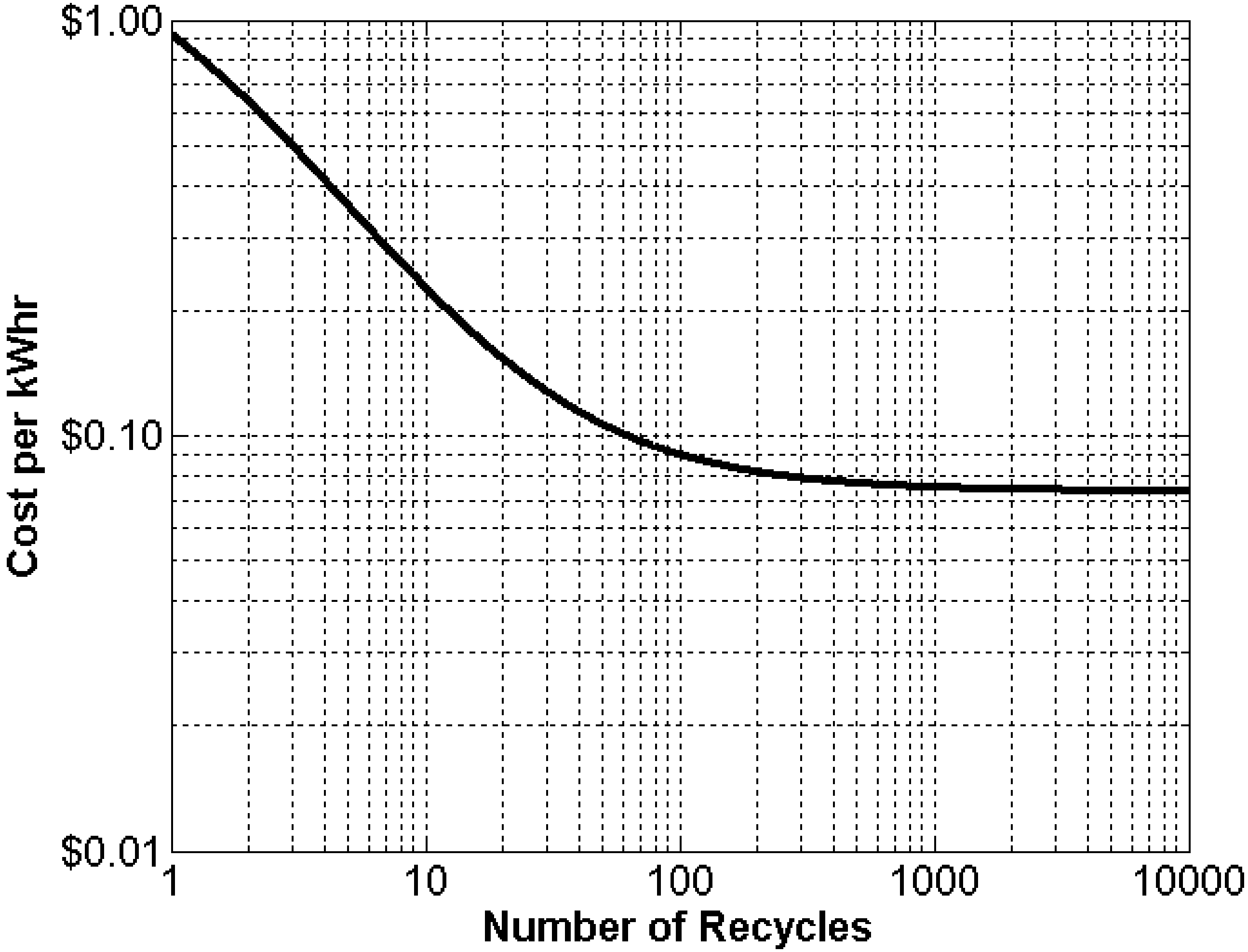
Economics

1. My conversation with the Alcoa folks in Australia provided me with an understanding of the cost of producing commercial grade Al.
2. Basic production of Al:

In order to make Al to customer's specifications, Alcoa refines bauxite until it becomes high purity alumina with an average particle size of 120 microns. This alumina gets shipped to the 9 foundries around the world where it is reduced to Al metal containing additive metals to customer specifications during the smelting process to reduce alumina to aluminum.

3. Cost of Al metal on the open market, $1.10 per pound.
4. Cost components per pound of Al.
   a. Bauxite mining and alumina separation - $0.20
   b. Alumina purification and particle sizing - $0.60
   c. Electrolysis of alumina to Al - $0.30
5. Energy content of 1 pound of Al: 4.1 Kwhr
6. Energy content of 1 pound of gasoline: 5.6 Kwhr
7. Cost of 20 lbs. Al; 1st lb @ rack price plus 19 recycles @ $0.30 = $6.80; Average cost per lb. = $0.34, i.e. for 1 lb of "new" Al recycle 19 times
8. Cost of 1 lb of Galinstan; 1st 0.05 lb @ rack price $125/lb. plus 19 recycles @ $0.05 = $7.20; Average cost per 0.05 lbs of galinstan = $0.36
9. **Cost of Al Alloy per Kwhr = $0.683/4.1 = $0.167**
10. **Cost of gasoline per Kwhr at $3.50/gal = $0.10**

Economics


$1.00
$0.10
$0.01
1
10
100
1000
10000
Number of Recycles
Cost per kWhr