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SOLID ALUMINUM ALLOYS: A HIGH ENERGY DENSITY MATERIAL FOR SAFE ENERGY STORAGE, TRANSPORT, AND SPLITTING WATER TO MAKE HYDROGEN ON DEMAND

Jerry M. Woodall

National Medal of Technology Laureate,
Barry and Patricia Epstein Distinguished Professor
School of Electrical and Computer Engineering,
Discovery Park Energy Center,
Purdue University, West Lafayette, IN 47906, USA

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Outline

- Energy density and technology sustainability
- Brief history and technology overview
- What else we know about it
- Process flow and hydrogen delivery control
- Markets and applications

Energy density and technology sustainability

Energy Density and Power Density

- As hydrogen from splitting water:
  - 1 Kg H_2: 142 MJ = 39.4 kW-Hrs combustible energy
  - 1 Kg Al* makes 111 gms. of hydrogen
  - 1 Kg Al makes 4.4 kW-Hrs as H_2 energy
  - 1 gal (10 Kg) Al makes 44 kW-Hrs as hydrogen
  - 1 gal. diesel: 37 kW-Hrs
  - 1 gal. liq.hydrogen: 10 kW-Hrs
- As heat from splitting water:
  - 1 Kg Al: 409 KJ x 1000/27 = 15.1 MJ = 4.2 kW-Hrs

* 1 Kg of water is converted by this process

Important facts about making aluminum

- Bauxite ore mined and dressed to extract alumina
- Alumina is chemically purified to 4-9s purity
- Purified alumina is sized to a powder with a particle size of 120 micrometers
- If done by Alcoa in Australia it is shipped to one of their nine smelters around the world
- Batches of Al with customer specified impurities are made by electrolysis of high purity alumina
- Spent Al products are mostly sent to scrap yards
- Most of this scrap Al metal with impurities is currently not recycled because it's cheaper to purify alumina than impure Al!

Technology Sustainability: large scale applications

World supply

- Al reserve in the planet's crust: about 10^{13} Kg (as Al); 1.2 x 10^{12} Kg of H_2 made by splitting water = 5 x 10^{13} kWhrs of H_2 energy
- Current worldwide annual Al production: 32 billion Kg from bauxite;
- ***400 billion Kg of impure elemental Al available for recycling!***

Large demand example: hybrid cars:

- If half of the impure "recyclable" Al was dedicated to split water, 50 billion Kg of H_2 could be made = 200 billion kWhrs (@ $0.15/kWhr)
- This could power a 100 million, 50 kW hybrid cars 200 miles

What about infrastructure/supply chain/vehicle fuel insertion?

- Some components either do exist or are easily realized
- Fuel insertion: 2-filler ports, one for water and one for alloy pellets both being hose delivered; spent fuel dumped into holding tanks

Brief history and technology overview

The Discovery

In 1968 Woodall discovered that aluminum (Al) dissolved in liquid gallium (Ga) just above room temperature would split water into hydrogen (H_2) and aluminum oxide (alumina) plus heat via the reaction:

$$2Al + 3H_20 \;-\!\!-\!\!> \; 3H_2 + Al_20_3 + heat$$


1 Kg Ga, 25 gms. Al, 100 C

Al in Ga Splitting Water to make Hydrogen!


3 days later

How does it work?

- Aluminum loves oxygen
- As a result, a skin of alumina (Al_20_3) forms on air-exposed pure Al and protects it from further rapid oxidation
- If this passivating oxide is disrupted, Al would react with water to produce hydrogen
- This can be done slightly above room temperature by dissolving Al into <u>liquid</u> gallium (Ga)
- When this liquid alloy contacts water, hydrogen is generated via Al in the Ga diffusing to the water-liquid metal interface where it splits water into hydrogen, alumina; the alumina is no longer protective

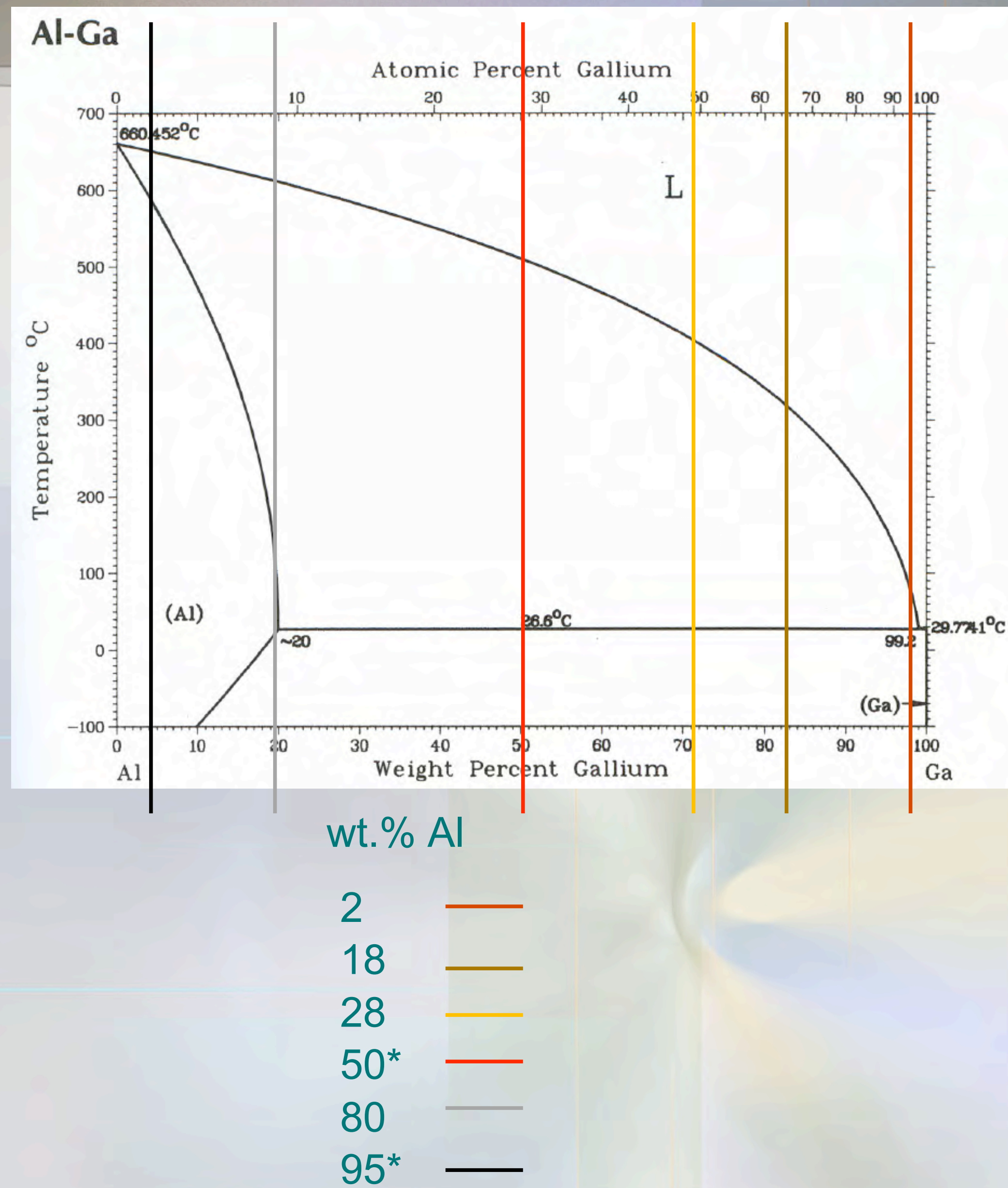
Where are we now?

- We can now make solid and bulk Al rich alloys (95 w% Al, 5 wt% Ga,In,Sn) that split water at temperatures between ice (0C) and steam (>100C) and make H_2 on demand

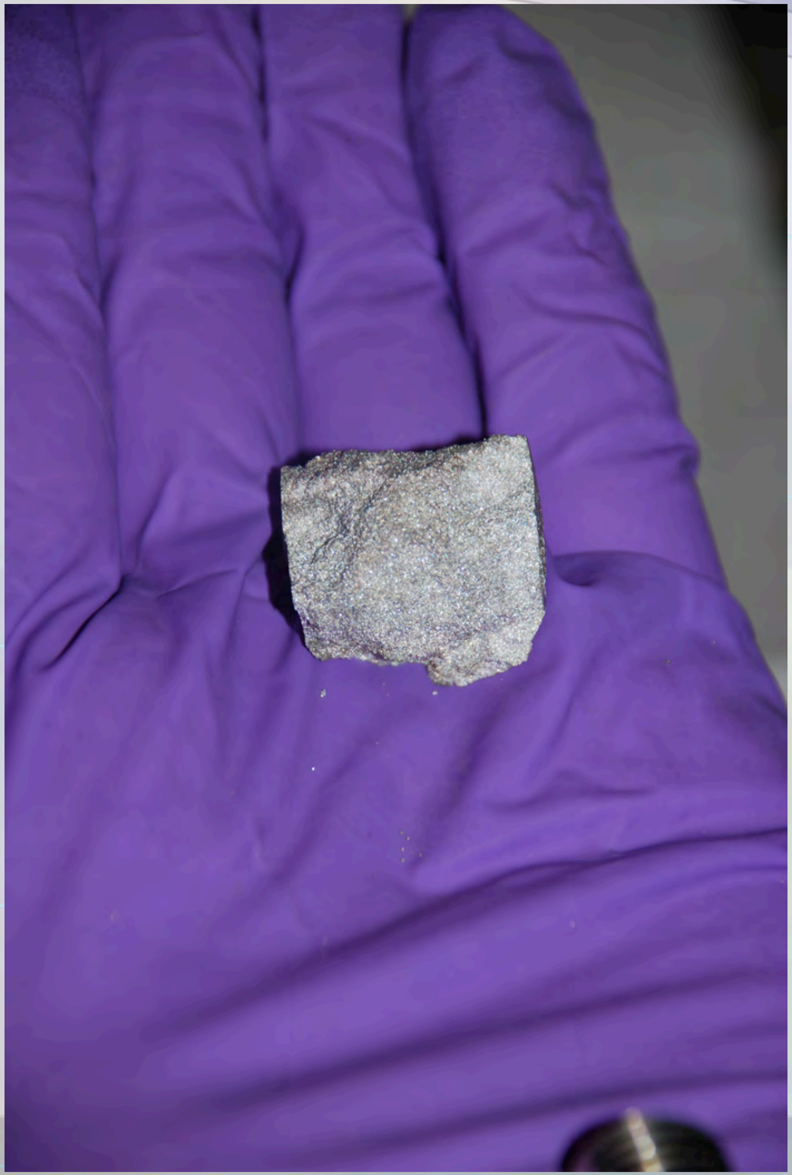
- 1st order *projected* materials cost of 20 cents per kilowatt hour of energy as combustible H_2 and 10 cents per kilowatt hour of energy as heat plus combustible H_2

Menu of water splitting Al alloys*

*These alloys substitute GaInSn for Ga

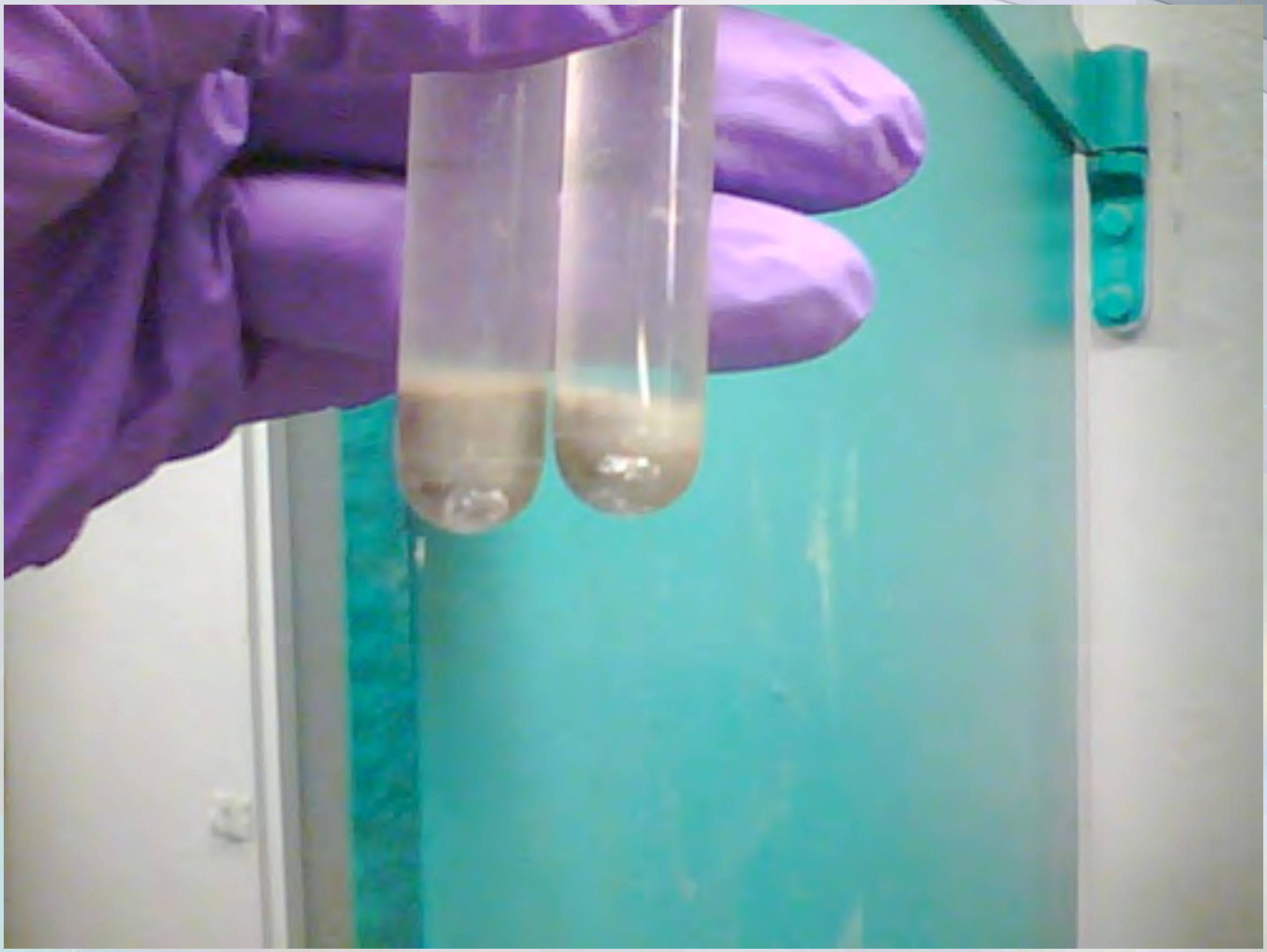


Internal sample of 95-5 Alloy from vender



A sample of 50-50 Al-GaInStan splitting water

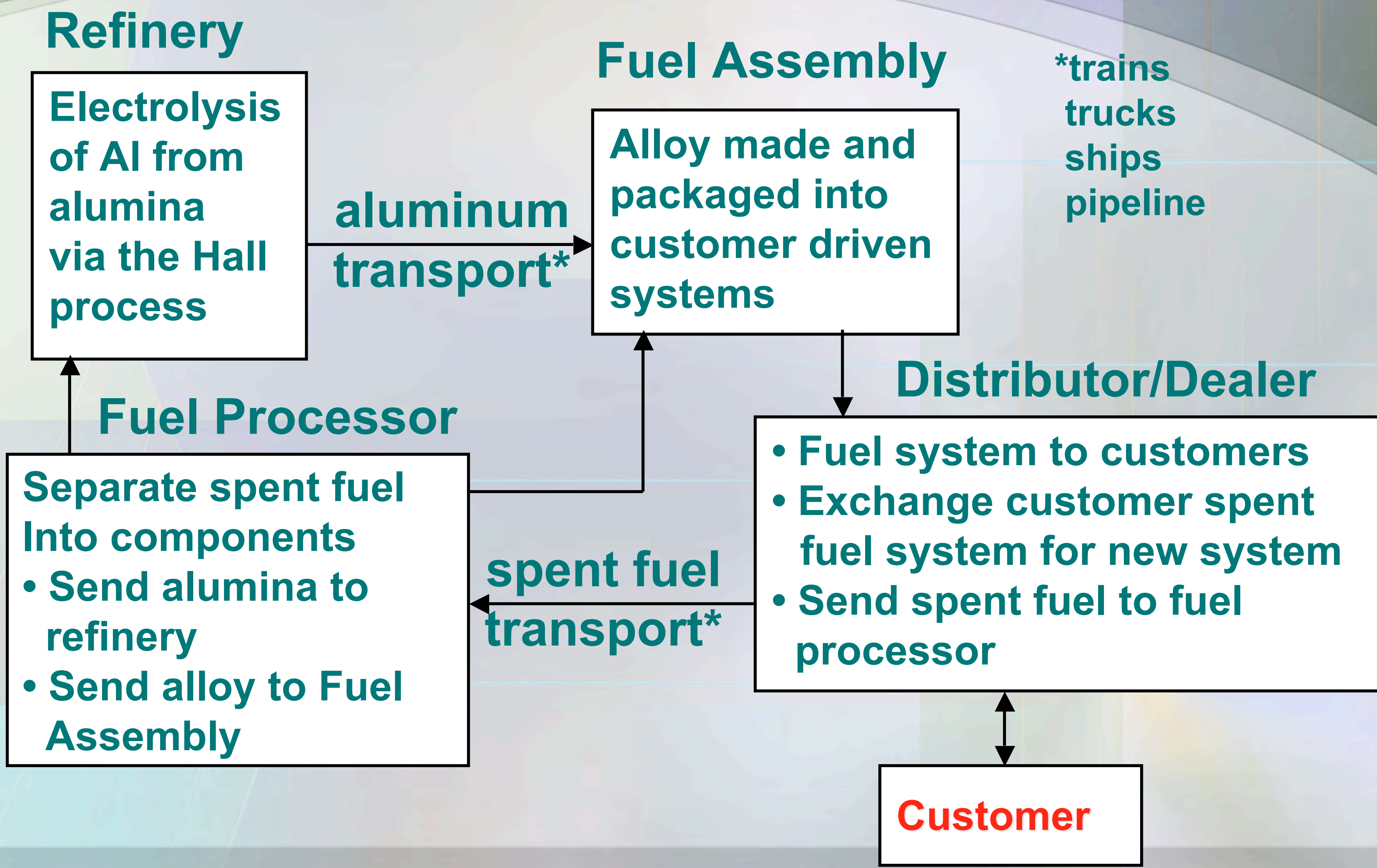
Complete centrifuge recovery of GaInStan alloy



What's the big deal?

- Technology is a path to enable the H_2 economy
- It can make H_2 on demand without storage or transport of hydrogen
- Energy used to make H_2 safely stored and transported as Al and generates H_2 by splitting water, and both Al and water are abundant
- Al, alumina and Ga,In,Sn can be of low purity, Ga,In,Sn totally recoverable/recyclable, Al_2O_3 electrolyzed to Al @ $0.66/Kg
- No external power or chemicals needed

A possible supply chain/infrastructure model



What else we know about it?

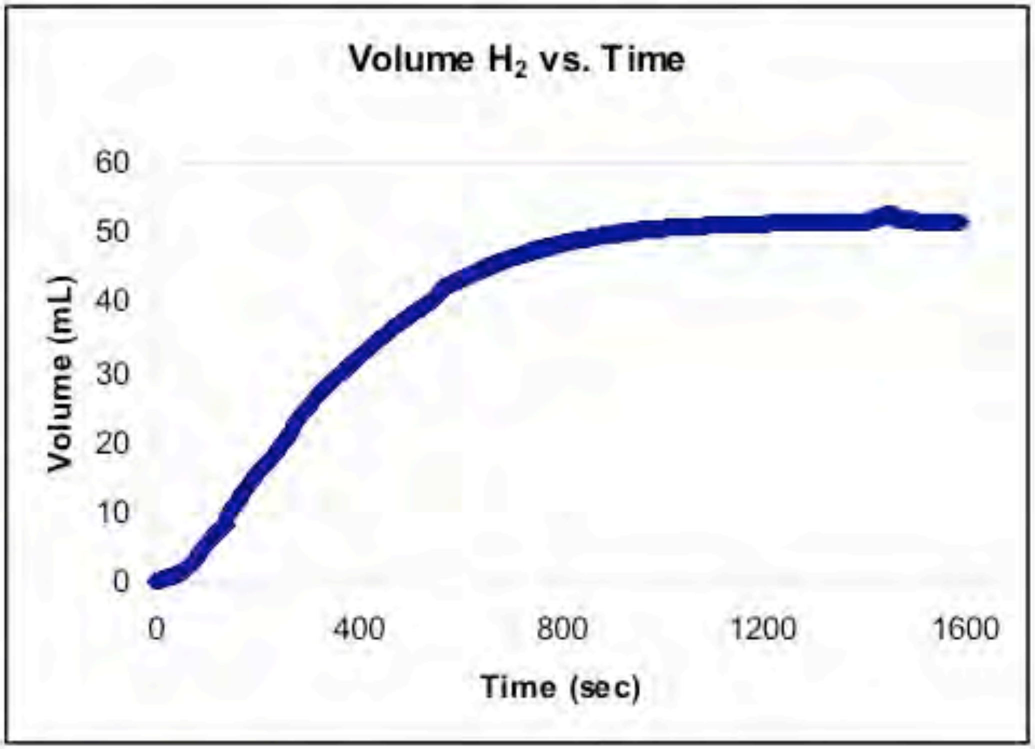
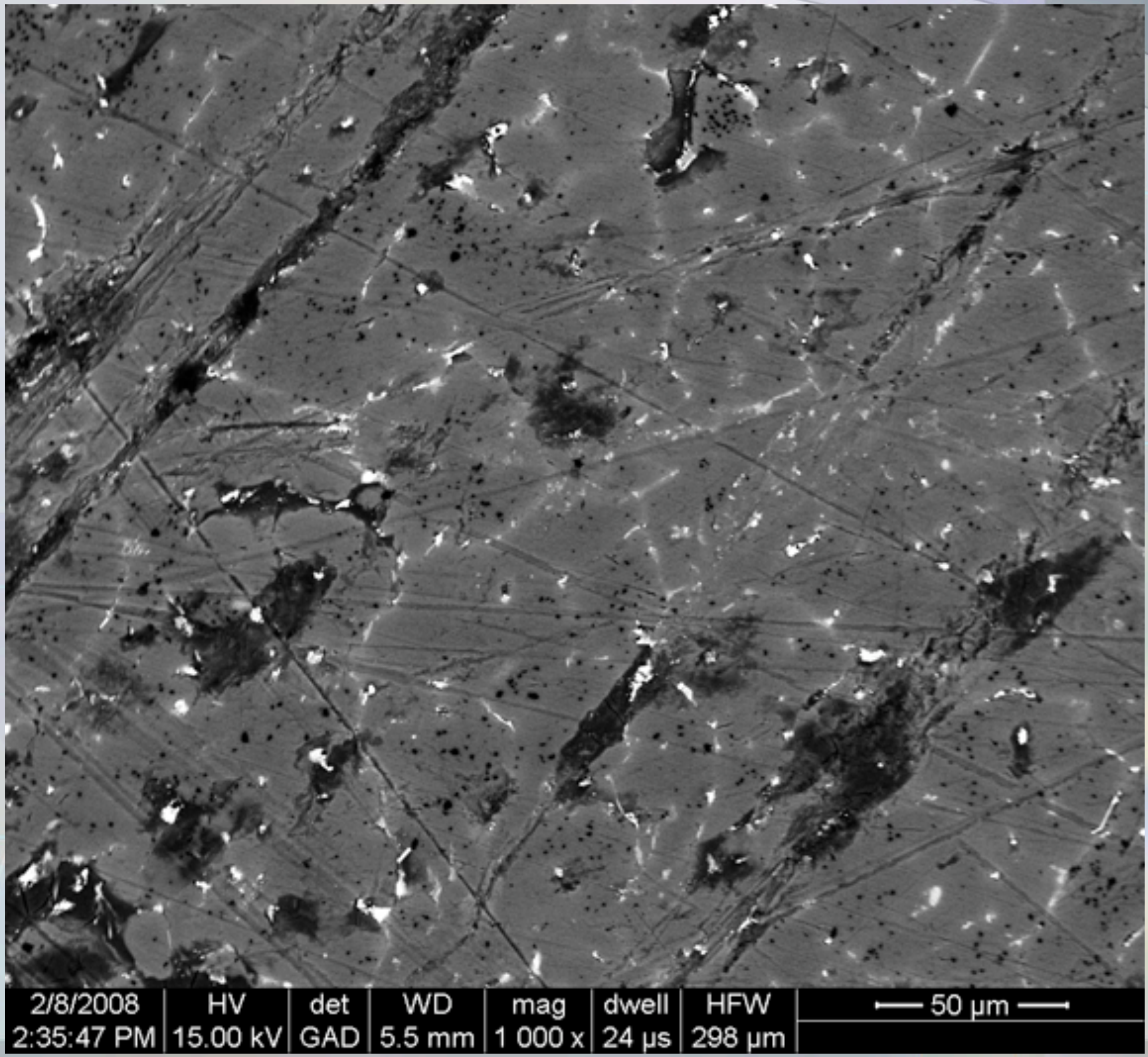


Figure 2: Hydrogen yield as a function of time

EDX mode photomicrograph of 95-5 sample showing In and Sn in the grain boundaries



So, how does the solid Al rich alloy split water?

We are not sure yet but our preferred model is:

the liquid Ga,In,Sn in the grain boundaries dissolves Al and this Al in solution splits water

Process flow and hydrogen delivery control

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Process flow and H_2 delivery control: research test-bed

- Prepare briquettes of 95-5 alloy from vendor
- Insert briquettes into "basket" in reaction tank, a 100 psi stainless steel paint pressure pot
- Reaction tank is valve connected to an Extrol expansion tank which is filled with water, valve closed
- Free space of reaction tank is evacuated and sealed
- Valve opened between Extrol tank and reaction tank
- Water flows from Extrol into reaction tank until in contact with alloy
- H_2 pressure builds up in reaction tank and pushes water back into Extrol tank until water loses contact with alloy
- Hydrogen flow controlled into engine via a buffer tank

Alloy briquettes

Experimental reactor and pressure controller

Up to 20 Kg of alloy (88 kWhrs of H_2)

Power: Al-water-H_2

Recent data shows that we can react 1 Kg Al in one minute = 15.8 MJ/min as H_2 (5% of a 20 Kg charge)

This converts into >250 kW of hydrogen power, and a power density of >125 kW/Kg(Al+water)

Challenges/issues

- Heat use/management
- Infrastructure/supply chain to manufacture alloys and recycle them
- Current energy efficiency is only 29%, i.e. energy from H_2/recycle energy x100 = 29% (industrial water electrolysis about 30%)
- If not recycled, the weight of needed water equals the weight of alloy used.

Markets and applications

Scale of possible applications/markets

- Small: 1-100 mW and 10 W-hrs, e.g. PDAs, laptops, i-pods, etc.
- Medium: 1-200 kW and 10-10000 kW-hrs, e.g. auxiliary power, cars, boats, fuel enrichment, etc.
- Large: >5000kW and > million kW-hrs, e.g. trains, ships, subs, off-grid community power, base load peak power demand, storage for wind and solar power

Possible application: replace batteries

Energy density (ED) of batteries:

lead-acid: 31-51 W-Hrs/Kg); Li-ion: 92-189 W-Hrs/Kg; Ni-metal-hydride (Prius): 59-119 W-Hrs/Kg

ED of Al-GaInSn(95-5)-$H_2$0 system as hydrogen:

1340 W-Hrs/Kg (Gibbs energy used for fuel cells)

Includes water weight, a 70% efficiency factor of fuel cells, but not container or fuel cell weight,(ED ratio is >>1 including weight of a high power fuel cell)

(ED Ga-Al-$H_2$0)/(ED lead-acid batteries)

>26! (>7 ED ratio for Li ion)

Possible applications/markets

Replace batteries with a Ga-Al-$H_2$0/fuel cell system for high energy density electric power applications:

- emergency/stand-by power (AlGalCo)
- electric wheel chairs
- golf carts
- PDAs, Laptops, etc.
- hybrid cars

Other applications:

- range extender (GM Volt?)
- liquid fuel multiplier, e.g. diesel enrichment
- trains, subs, trucks
- large boats and other maritime applications
- desalinated/potable water!

Electricity costs to reduce Al^{+3} to Al

- The electrochemistry of reducing Al (in alumina) is: $Al^{+3} + 3e^{-} \rightarrow Al$, and requires about 15 kW-hr/kg of Al at a present process efficiency of 50%

Using autos with ICEs for example:

- 2.9 Kg. Al will produce the same amount of energy in the form of hydrogen as 1 Kg of gasoline, i.e., 42 K BTU
- It takes 20 gal. x 2.7 Kg/gal = 54 Kg gasoline to drive a midsize average car 350 mi, or 157 Kg, Al*
- At $3.50/gal for gasoline and $2.40/Kg for Al, the trip costs $70 using gasoline and $380 using Al (ouch!)

*63 Kg. on-board water will be required, assumed to be a negligible cost and a 60% recovery rate (DOE number) for continuous reuse

Costs to reduce Al+3 to Al (cont.)

For an Al recycler next to a nuclear power plant* with an on-site power cost of $0.02/kW-hr, the Al can be recycled from alumina back to Al for:

15 kW-hr/Kg x $0.02/kW-hr = $0.30/Kg of Al**

2.9 Kg Al production cost is about **$0.87 ($47/trip)**

$3.50/gallon, (retail) 1 Kg of gasoline costs **$1.30 ($70/trip)**

For equal energy (as H_2) Al can be cheaper than gasoline; so its all about weight

*For the future, Al recycling could be done at solar photovoltaic farms and/or wind turbines sites.

**The Al smelted by electrolysis has a CO_2 ratio of 1/3 compared with CO_2 from burning gasoline. However, this CO_2 could be sequestered

On-board H_2 mass density for the 95-5 Al alloy

$$2Al + 3H_2O \rightarrow 3H_2 + Al_2O_3$$

To get 6 mass units of H we need:

- 54 mass units of Al
- 48 mass units of O
- 3 mass units of "catalytic" Ga,In,Sn

The total source mass units = 54+48+6+3 = 111, and the on board H mass density = (6/111)x100 = 5.4%.

However, the only on-board source required in full at the beginning is the Al+alloy; the source of H and O can be added dynamically via H_2O recovery. Assuming a 50% recovery of H_2O, we get an H density of (6/84)x100 = 7.1% at the beginning and (6/102)x100 = 5.9% at the end or an average density of 6.5% (>DOE 2010 goal)

Costs to reduce Al+3 to Al (cont.)

Oh, if only there were a reliable fuel cell technology that could deliver 150 KW for $10/kW

For a fuel cell plus electric motor powered car:

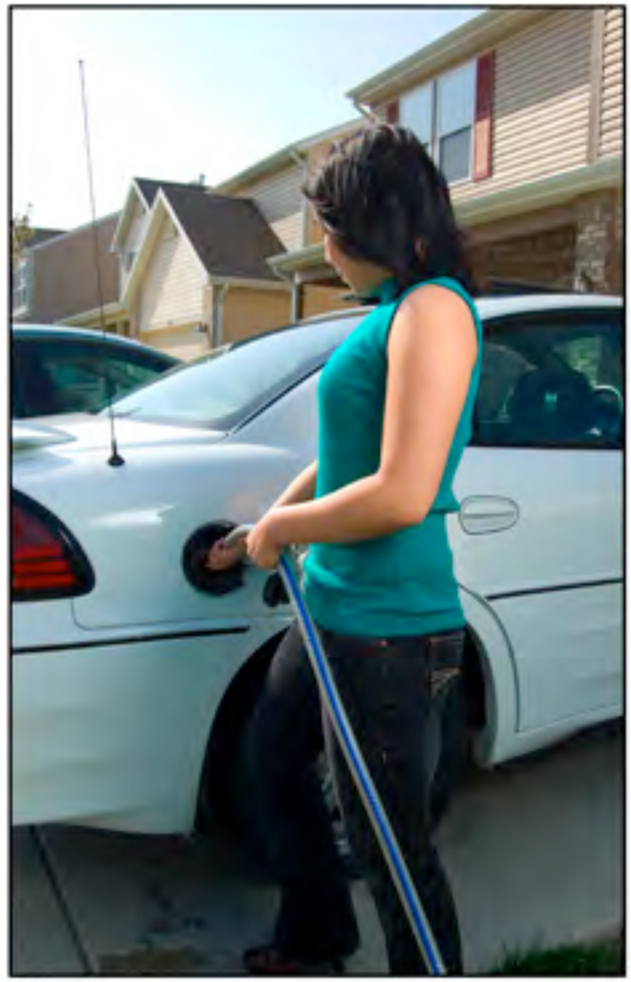
If we assume a fuel cell plus electric motor efficiency of 64% only 1/3 of both the weight of Al plus water will be needed, i.e. 0.33 x 157 Kg plus 0.33 x 63 Kg water = 52 + 21 = 73 Kg. compared with 54 lbs of gasoline for an ICE powered car.

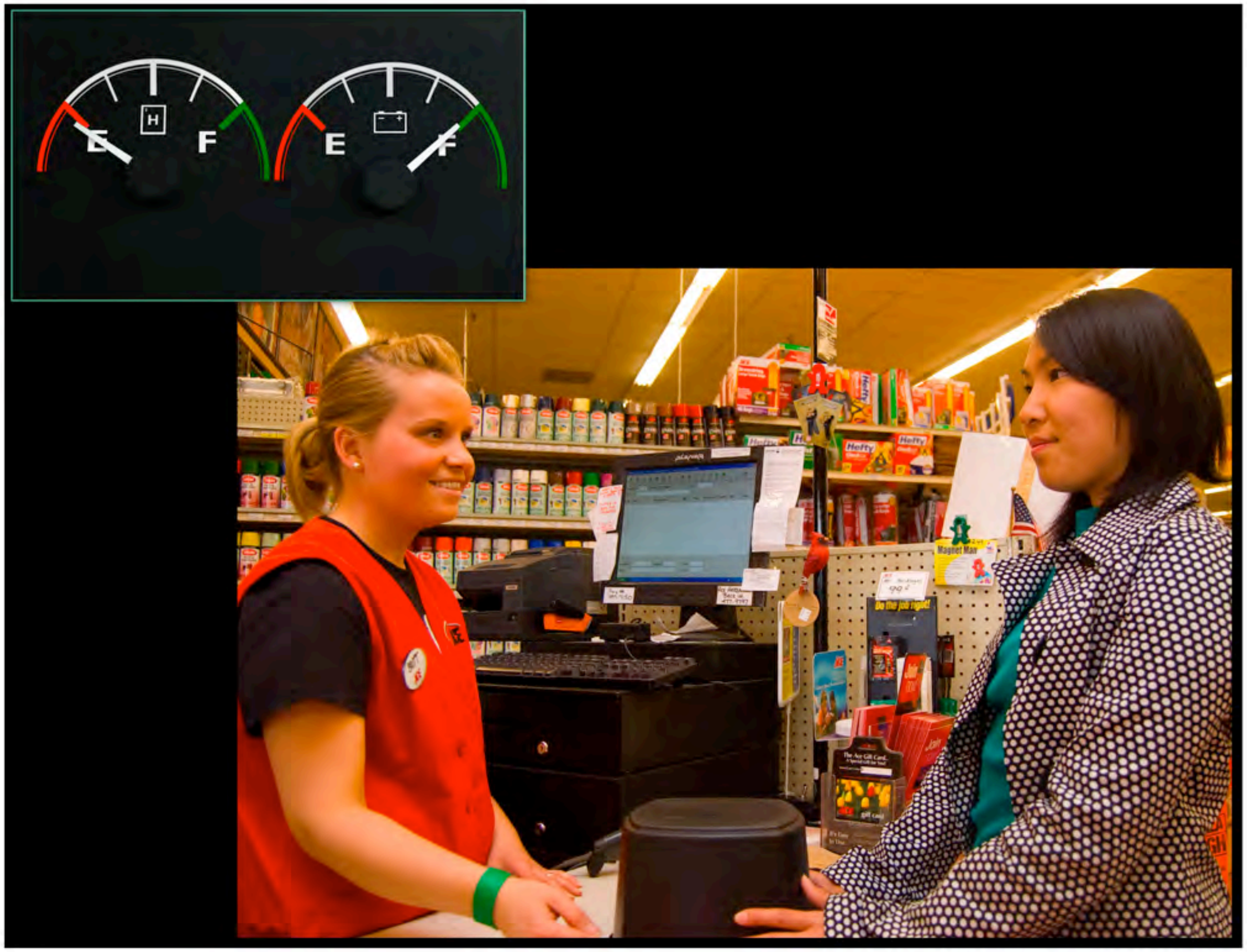
$0.30/Kg x 52 Kg. = $16.00 per 350 mi. trip (wholesale)

A Possible Model for the Volt: GM's First Hydrogen - EV Hybrid Car

Assumptions:

1. A 40 KW ICE tuned for hydrogen and an efficiency of 60 mpegg to drive a generator as the batteries run out
2. 13 kWhrs of hydrogen needed to drive 20 miles
3. 3 Kg of alloy will generate needed hydrogen, alloy contained in a "canister" plugged into fixture in trunk
4. 3 Kg water water "hosed" into the gasoline filler port
5. Canister exchange: e.g. convenience stores, Walmart, car dealers, etc.; spent canister sent to refineries, recharged and returned to distributor; GM internal business model not part of supply chain

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Start up: EV-H_2 hybrid model

- Normal case: batteries are charged - no issue
- Worst case: batteries are discharged and no hydrogen in a buffer tank; how long will it take to start the car?
- 4.4 kWhr of H_2 energy can be generated in 1 minute, I.e. > 250 kW available power for one minute

Advantages for GM and the Volt model

- First GM EV-Hydrogen Hybrid Car
- Infrastructure, distributed, diverse and in place, e.g. Alcoa, Walmart, convenience stores, gas stations, dealers, etc.
- GM does not have to make the supply chain part of their internal business model
- Current Volt model, 40 mile range using batteries, as the primary power source. Auxiliary power use intermittent.
- Gasoline degrades in the tank without use but Al alloy does not.

H_2 enrichment of diesel fuel model - cars

- 15% H_2 enrichment of diesel gives 30%* increase in efficiency
- No Blutech needed to get rid soot or Nox
- Assume 40 mpg car with a 10 gal. diesel fuel tank;100 gal. of diesel needed for 4K miles and an oil change required after 4K miles; cost of 100 gal. diesel: 100 gal. x $4.35/gal. = $435
- Weight alloy needed for 4K miles: 100+ kg; weight of water: 100+ kg
- Total cost per 4K miles boosted 30%, with Al-H_2 technology: $411. Canisters swapped out during oil change operation
- Spent alumina removed at 4K mile intervals along with oil change

* Not a vetted number

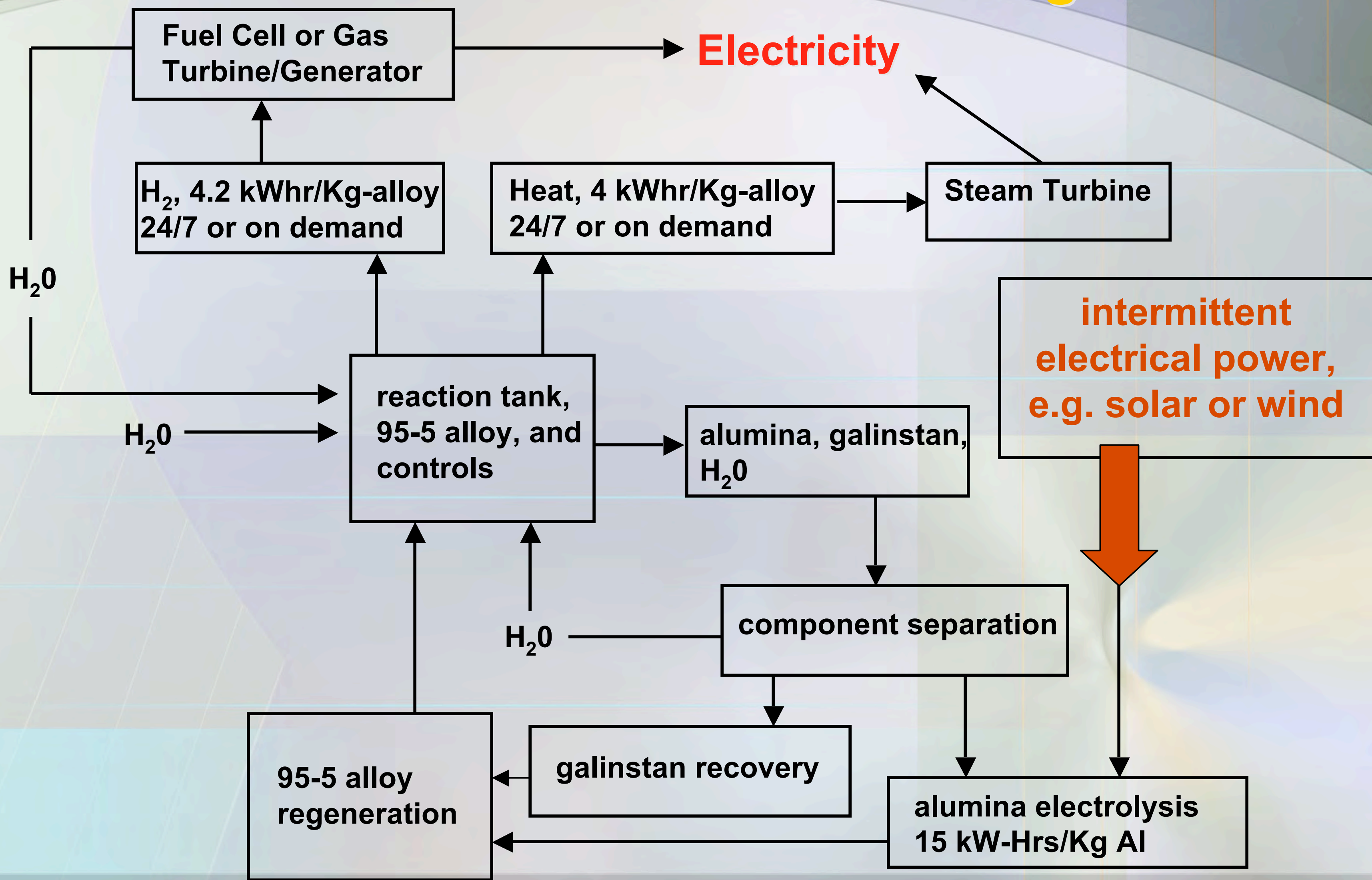
H_2 enrichment of diesel fuel model - trains

- 60,000 gal. train oil tanker with 95-5 Al alloy; (2.5 million kW-h as H_2)
- Al tanker connected to 60,000 gal. water tanker both trailing train engine
- A 50 car loaded train runs on a 4000 peak horsepower diesel-electric engine, 2000 average rolling HP, i.e. 1,500 kW, or 110.6 Kg of diesel/h
- Train use: 4 Kg of hydrogen per hour made from the Al alloy = 157.6 kW-h
- Al Tanker can generate 15,900 hours worth of hydrogen or over 660 days of continuous generation!!!
- To use all the energy a heat exchanger makes steam from water in an extra tanker and drives an additional dynamo.
- Or react the alloy in super heated steam and feed steam plus hydrogen into closed loop turbine, condense and reuse water and separate out hydrogen as input diesel electric engine.
- Value proposition: H_2 enrichment via splitting water with Al is “free”!

Another possible application:

- Enabling Wind or Solar as Base Load Electricity Generation Capacity
  - Target cost: $0.10/kWhr, assuming 40x alloy recycling
  - All required technologies are known
  - Primarily an Engineering Development Project
  - Enables Environmentally Sound and Secure Electricity

Enabling Wind or Solar as Base Load Electric Power Model Flow Diagram



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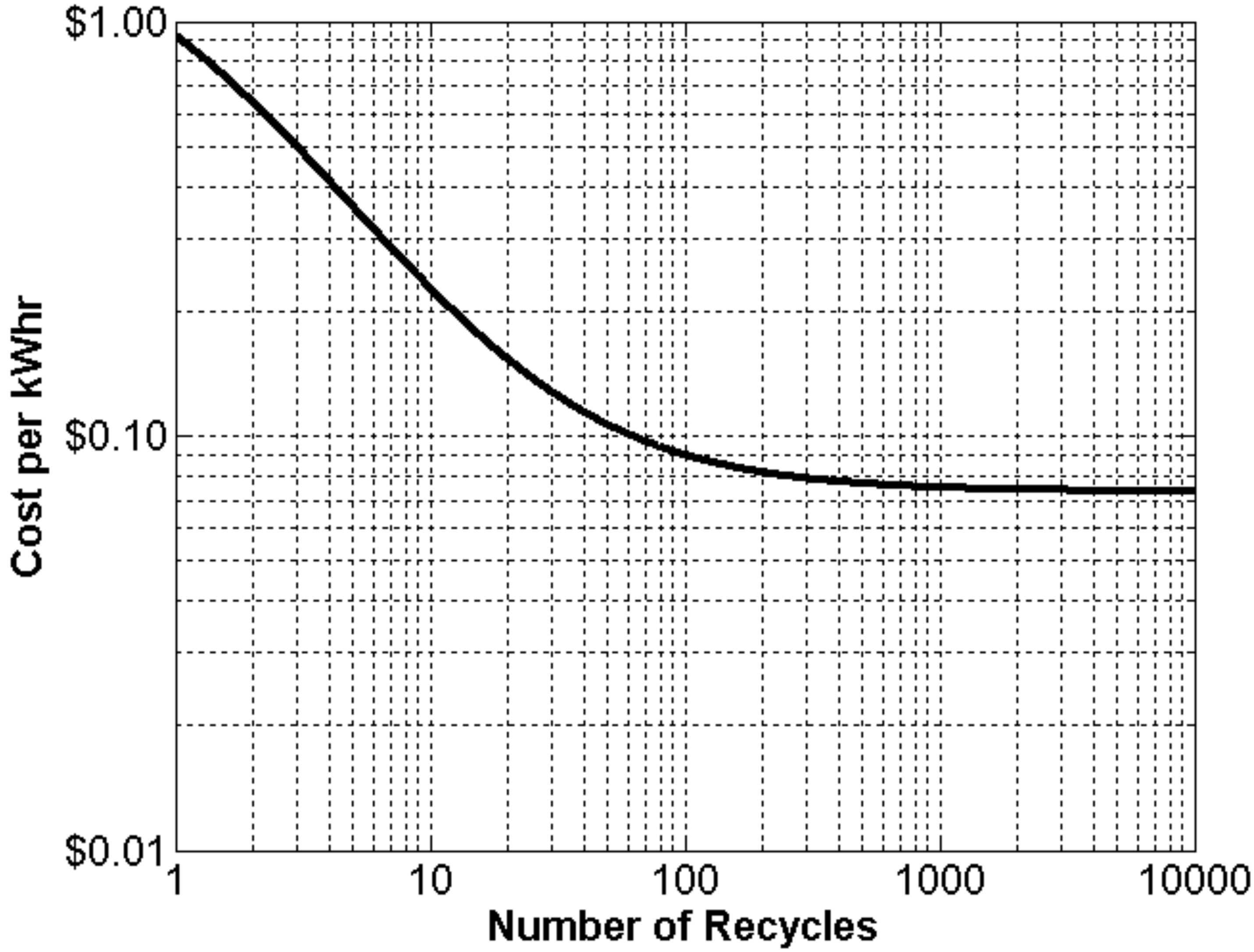
1st order economics of our process

- Cost components per pound of Al @ $2.42/Kg (retail)
  - a. Bauxite mining and alumina separation - $0.44
  - b. Alumina purification and particle sizing - $1.32
  - c. Electrolysis of alumina to Al - $0.66
- Energy content of 1 Kg of Al: 8.6 kW-Hrs
- Energy content of 1 Kg of gasoline: 12.3 kW-Hrs
- Cost of 20 Kg. Al; 1st Kg @ rack price plus 19 recycles @ $0.66 = $15; Average cost per Kg = $0.75
- Cost of GaInStan; 1st 0.05 Kg @ rack price $250/Kg plus 19 recycles @ $0.10 =$14.40; Average cost per 0.05 Kg of GaInStan = $0.72
- Cost of Al Alloy = ($1.47/8.6 kW-hr) = $0.17/ kW-Hr
- Cost of gasoline @ $3.50/gal = $0.10/kW-Hr

Cost of total energy vs. number of alloy recycles



What about gallium and GaInStan?

- Ga,In and Sn are inert and totally recoverable.
- Experiments have recycled the Ga used in water splitting solid alloys up to 32 times.
- Currently, the 60 ton market for Ga is for electronics with purities between 4 and 7-9s, about $0.35/gm!!!!!
- Our process runs on low purity Ga,In,Sn and low purity Al and tap water/non potable water.
- Our analysis shows that with multiple reuse, a price of the alloy component charge of $0.70/kg can be realized.
- For fuels with <5% Ga there is enough economically recoverable Ga to run 10^9 cars.

Bottom line:

- No technical show stoppers for large scale use of of Al rich solid alloys splitting water to make hydrogen and heat on demand

- However, there are plenty of barriers to realize it including
  - US government agencies, especially DOE
  - The fossil fuel and an motor vehicle industries
  - The $100 billion needed to build the infra-structure