High Flux Metallic Membranes for Hydrogen Recovery and Membrane Reactors

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REB Research & Consulting

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REB Research & Consulting
Hydrogen Separations and Membrane Reactors

PD19

Overview

Timeline

- October 1, 2005- September 30, 2008
- 50% complete

Budget

- Total project: $2,919,857
  - DoE: $2,334,646
  - REB+ ISU: $ 585,211
- DoE funds '06: $474,505
  - Non DoE '06: $ 85,929
- DoE funds '07: $886,206

H_2 Barrier addressed

- **Lowering the cost/flux H_2 permeation membranes. This lowers the cost of H_2.**
  - Replace palladium with base metals: $100/ft^2 vs $3000/ft^2
  - 100% selectivity like Pd
  - 50 scfh/ft2 UHP H_2 at ΔP=200psi
  - 15+ life, no embrittlement

Partners

- **Iowa State U.:** Helps pick alloys, x-rays
- **Ames Lab:** Makes alloy samples
- **LANL:** Coats, welds alloys, some tests
- **NETL**: Permeation and life tests
- **G&S Titanium Co.:** Fabricate membranes
- **REB Research: Management and assembly**

Who Does What?

- Allan Russell, Iowa State, helps REB pick the alloy; does x-ray analysis, Instron tests.
- Larry Jones, Ames Lab - Materials Preparation Center makes up the alloys in disc and striker form; manufacturability.
- Robert Buxbaum, REB Research embrittles the alloys; Charpy test of embrittlement; braze tests; assembly of bundles, flux test; management, commercialization.
- Steve Paglieri, LANL, coats the alloys, does some permeation tests, and oversees welding into tubes, life analysis.
- Mike Ciocco, NETL, oversees most permeation tests and basic life tests.
- Rodger Geiser, G+S Titanium, draws the welded tubes into membranes

We aim to make hydrogen so cheaply that only the very rich will use bottled gas

- REB Research is the only company making commercial membrane reactors.
- This membrane reactor unit reforms $CH_4OH + H_2O$ and outputs 3.5 slpm of ultra-pure hydrogen for laboratory use.
- Our generator design was developed in a phase 1 SBIR grant.

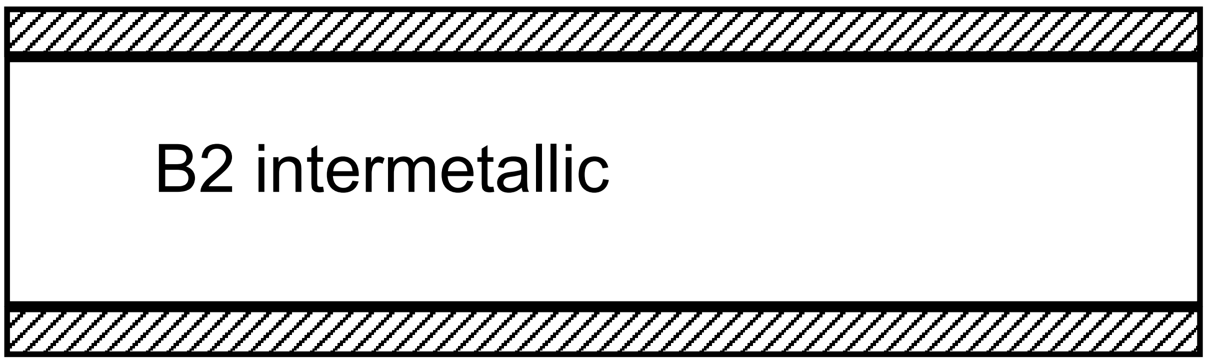
Project Objective:

- **Find a base metal replacement for palladium ($470/oz) and for our own sandwich membranes for use in hydrogen purifiers and membrane reactors.**
  - Stable at 350- 400°C
  - 100% selectivity like Pd
  - $100/ft^2 vs $3000/ft^2
  - 50 scfh/ft2 UHP H_2 at ΔP=200psi
  - 15+ life, no embrittlement

Approach: make sandwich membranes

REB's US Patents 5,108,724; 5,149,420; and 6,576,350.

Pd alloy coat; 0.5μ thick

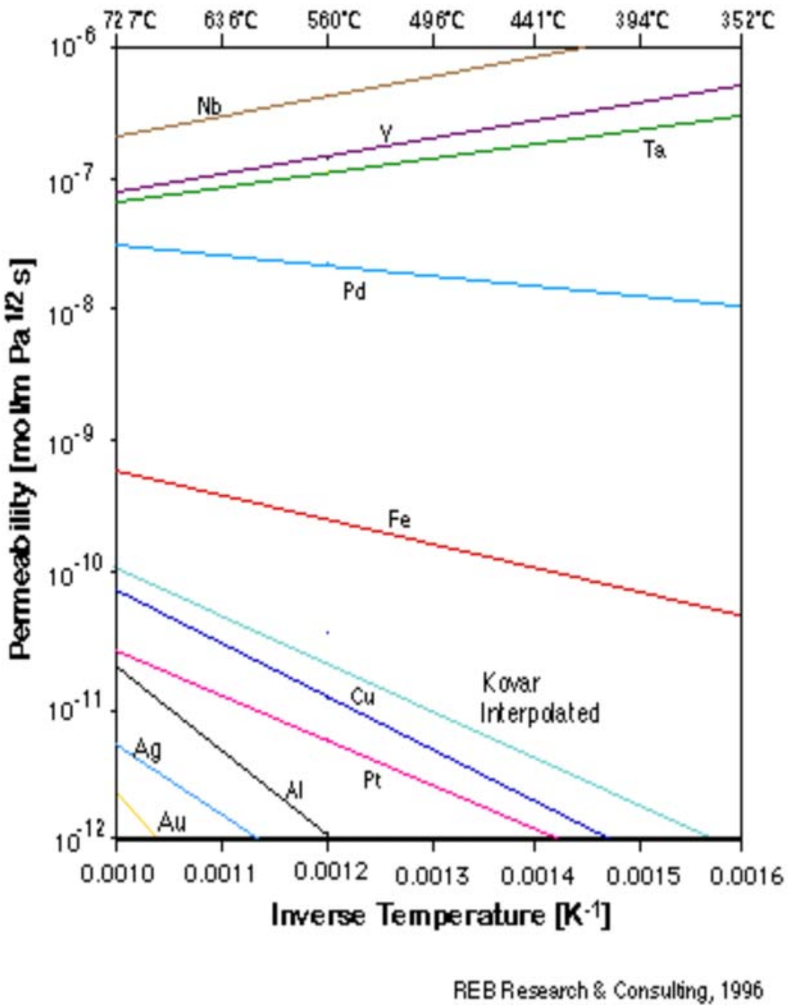


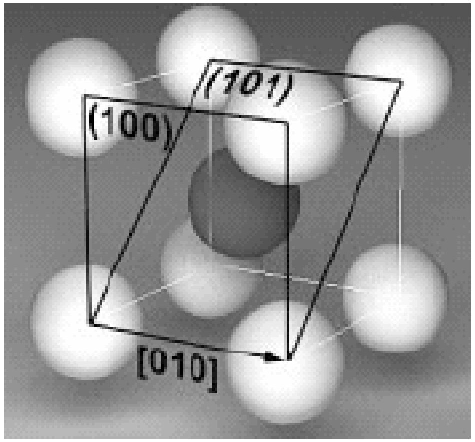
Pd alloy coat; 0.5μ thick

With some alloys, the coat is not needed

US Patent applied for

Accomplishments: Pick B2 alloys





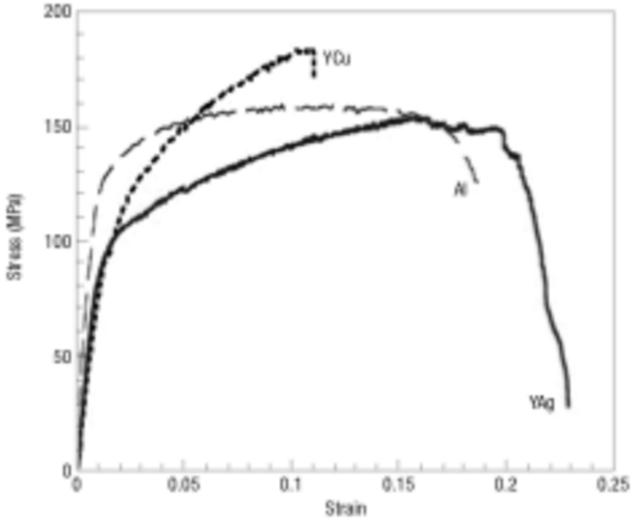
At left, note that several metals: V, Nb, and Ta have 100 times higher permeabilities than Pd at 350-400°C They cost only 1/100 as much as Pd. Unfortunately they embrittle in H_2.

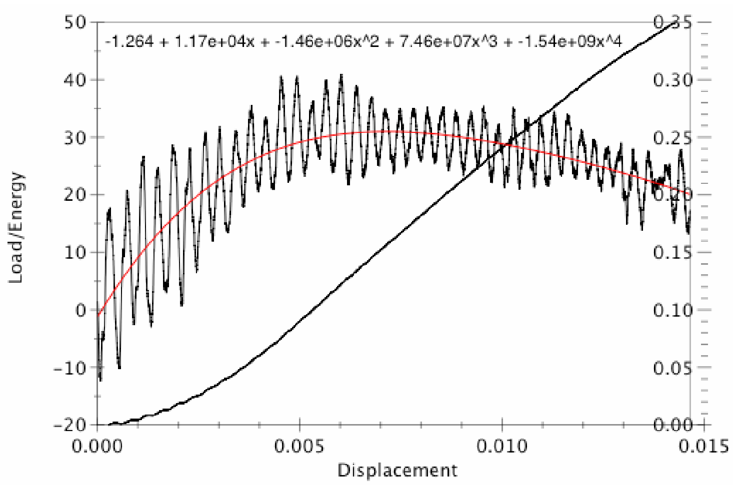
Our approach is to try B2 intermetallic alloys, like NiTi (above). So far we've tried about 60. We'd previously noted high interdiffusion and embrittlement in B1, random BCC alloys

Allan Russell (ISU) a key helper here Ames Lab makes the alloys

We aim for stable, ductile B2 alloys that we think will pass H_2

Roll and cut into discs (Ames Lab)
Coat with a thin Pd layer (LANL)
Measure mechanical properties (REB Res., ISU)
Hydride and then measure mechanical properties (REB Res)





Two newly discovered, ductile B2 alloys
Al 3105 shown for comparison.
Alloys are ductile to over 20% strain

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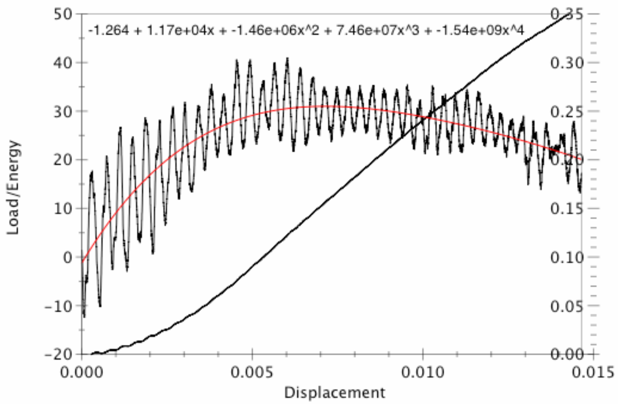
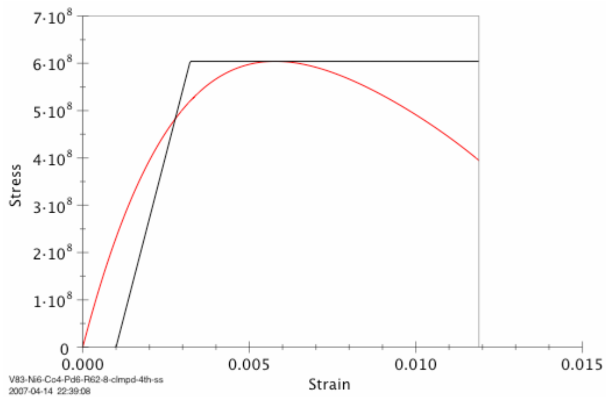
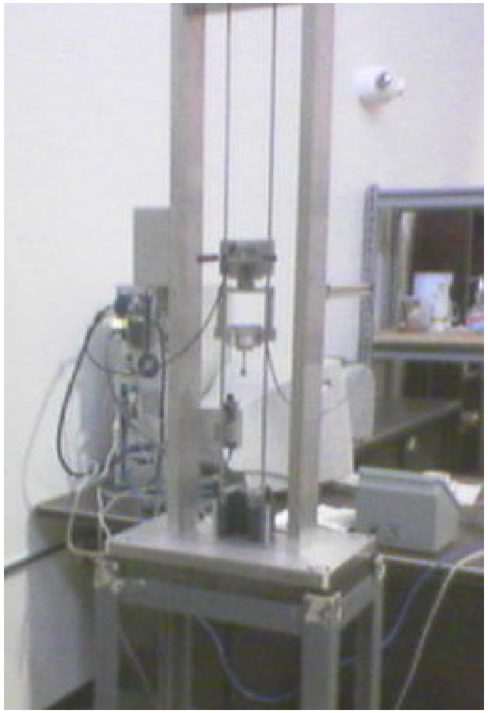
Charpy Mechanical Tests

Hit it with an instrumented Charpy hammer. If it breaks it's brittle.

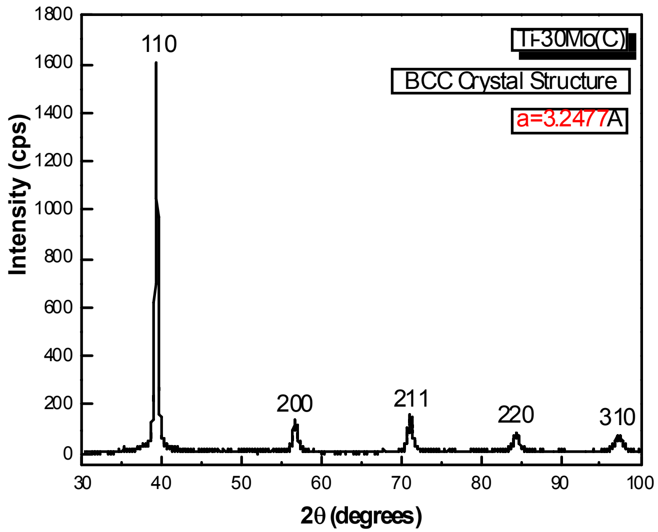
•Determine stress-strain curve before and after hydriding



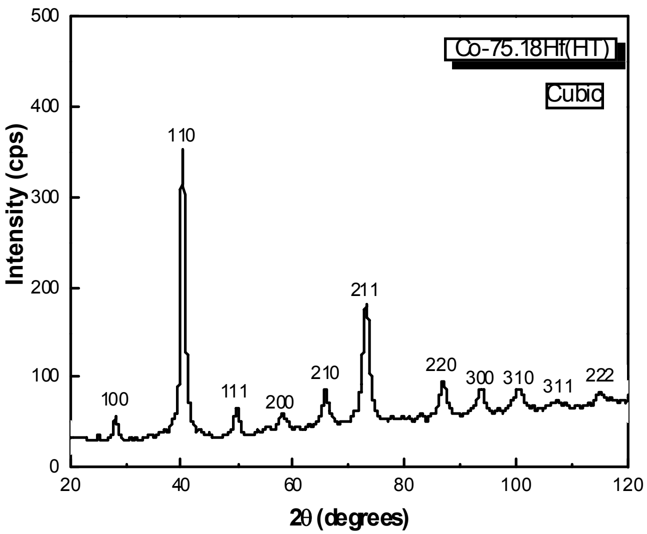




X-ray pictures

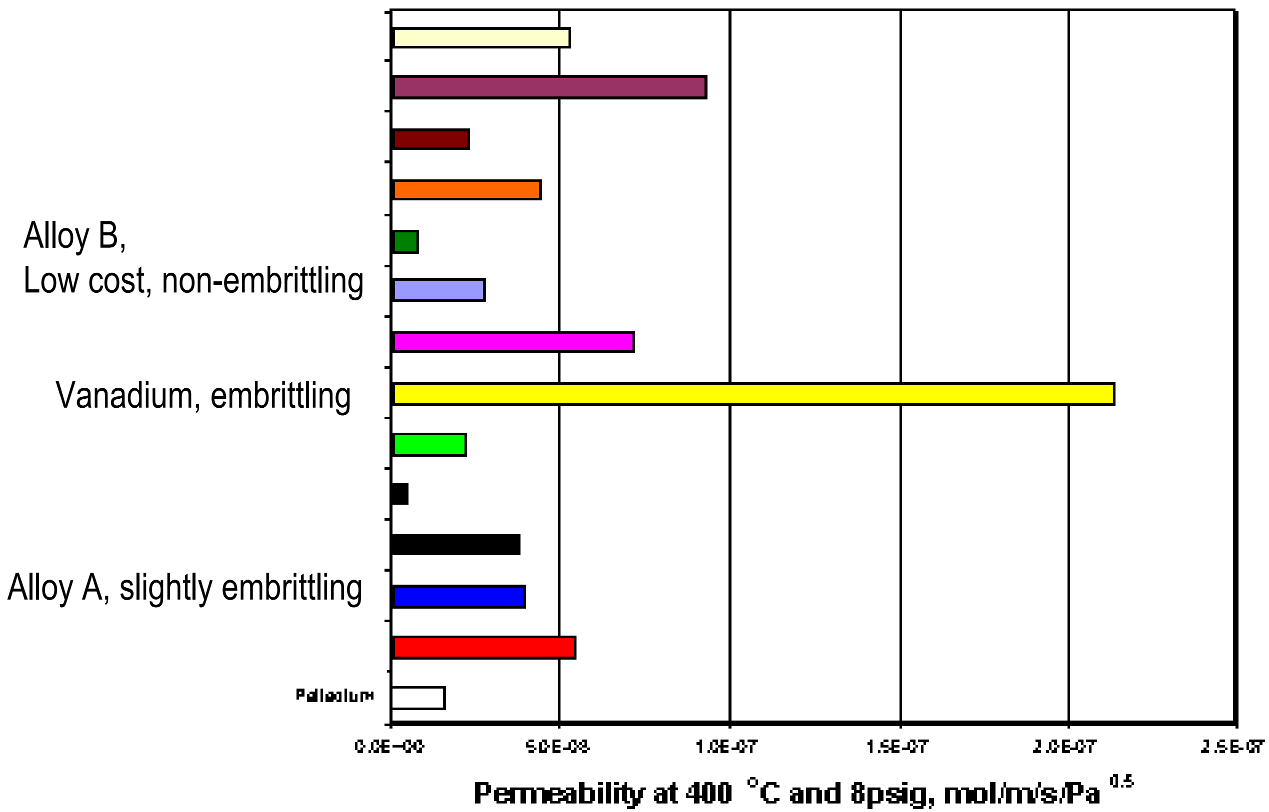


Random BCC structure



B2 cubic structure

Result of Hydrogen Permeability Measurements



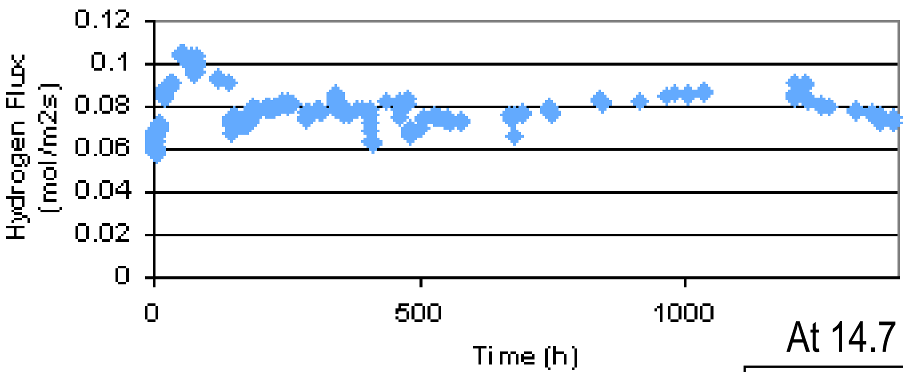
Lifetime Tests: Flux versus time for alloy “A”

Accelerated aging test

400°C, 46 days 0.1µ coat

> 0.2 mol/m2s (51 scfh/ft2) at ^{2}P= 44 psi.

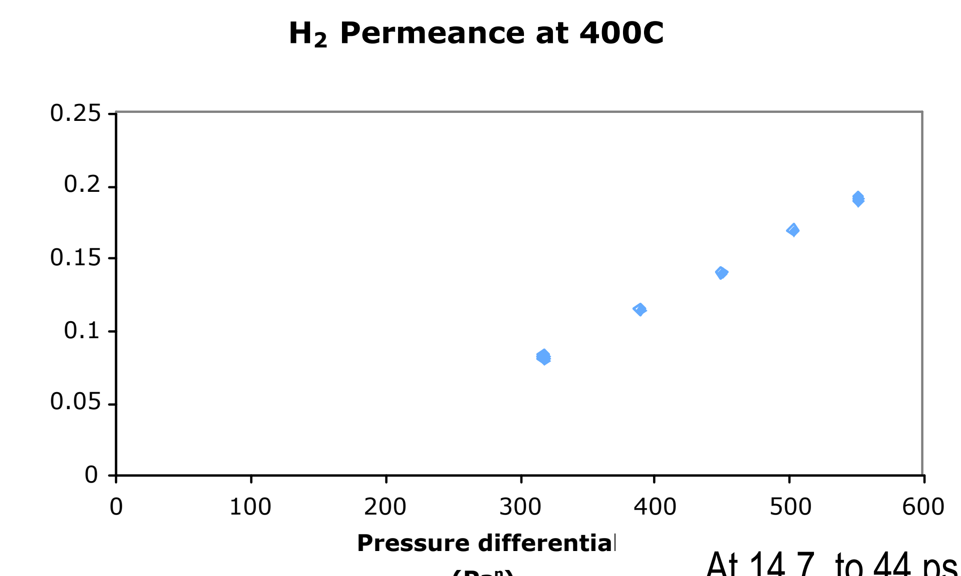
Equivalent of 250scfh at 200 psi; 15 years at 1.1µ coat



At 14.7 psi

- We met the target flux at 1/5 the target pressure, suggesting 3 or 4x the target flux at 200psi
- Accelerated lifespan measured, as we planned, with a thinner Pd coat. Life meets project targets.

- Price of this membrane about \$95/ft^2 meets targets
- Membrane broke when temperature lowered below 200°C under pressure. Not robust enough for most industrial uses. OK for nuclear use at low P.



At 14.7 to 44 psi

Brazing experiments:

For the alloy to be worthwhile, it must be possible to fabricate hydrogen purifiers from it: should braze to stainless steel.

- Try lots of brazes connecting SS to alloys in tube and sheet form.
- Two successful brazes shown below.

Accomplishments, year by year

2005	Pick first alloys, mostly B2. Use base metals so $100/ft^2 is likely Buy equipment	Done Done
2006	Test for manufacturability and embrittlement of first 50 alloys using Charpy hammer Test flux: want 50 scfh/ft^2 at 400°C, 200 psi	Exceeded: 82 alloys 51scfh/ft^2,44psi
2007	Test life accelerated aging: want 15 years Make another 50, better alloys Test for permeation and embrittlement Test brazing and welding; make first tubes	40% done 70% along 30% along 30% along
2008	Make tubes of best 2 alloys Make and test membrane reactor Final report, begin commercialization	0% 0% 5% along

Technical Accomplishments:

We found several "almost" alloys

Among our "misses" are alloys with other valuable properties: one that seems like Pt; another like aircraft Ti, but 20% lighter; another like aircraft Ti, but with a 200°C higher creep temperature. These may be good for catalysis, aircraft, 4th generation nuclear, or prosthetics.

- **We have 2 publications, and more in works and we keep working on alloys for the next 18 months.**

- **Lowering the cost/flux H_2 permeation membrane lowers the cost of H_2**
  - Replace palladium with base metals: \$100/ft^2 vs \$3000/ft^2 √
  - 100% selectivity like Pd √
  - 50 scfh/ft2 UHP H_2 at ΔP=200psi √
  - 15+ life √
  - no embrittlement (1/2 - not for high flux)
  - Welding + manufacturing (1/2 done)

Future Work (2007)

- "Tweaked" alloys: for high flux, no embrittlement (ISU, Ames)
- Continue to make welded tubes (LANL)
- Draw tubes into membranes (G+S)
- Continue braze tests (REB)
- Fabricate and test as purifier, membrane reactor (REB)
- Confirm that behavior matches flux, cost, and durability goals (REB, LANL)

Summary

We aim to make hydrogen so cheaply that only the very rich will use bottled gas

Figure 9: Membrane reactor hydrogen generator made by REB Research. Only two other companies make similar product Tokyo Gas and Idatech; Idatech licenced from REB.

Make hydrogen,$250/MMBtu, from methanol, $16MMBtu,

- **Lowering the cost/flux H_2 permeation membrane lowers the cost of H_2**
  - Replace palladium with base metals: $100/ft^2 vs $3000/ft^2 √
  - 400°C Operation
  - 100% selectivity like Pd √
  - 50 scfh/ft2 UHP H_2 at ΔP=200psi √
  - 15+ life √
  - no embrittlement + high flux not yet

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Thank you for your support!

Additional Slides

Questions?

Contact: Robert E Buxbaum

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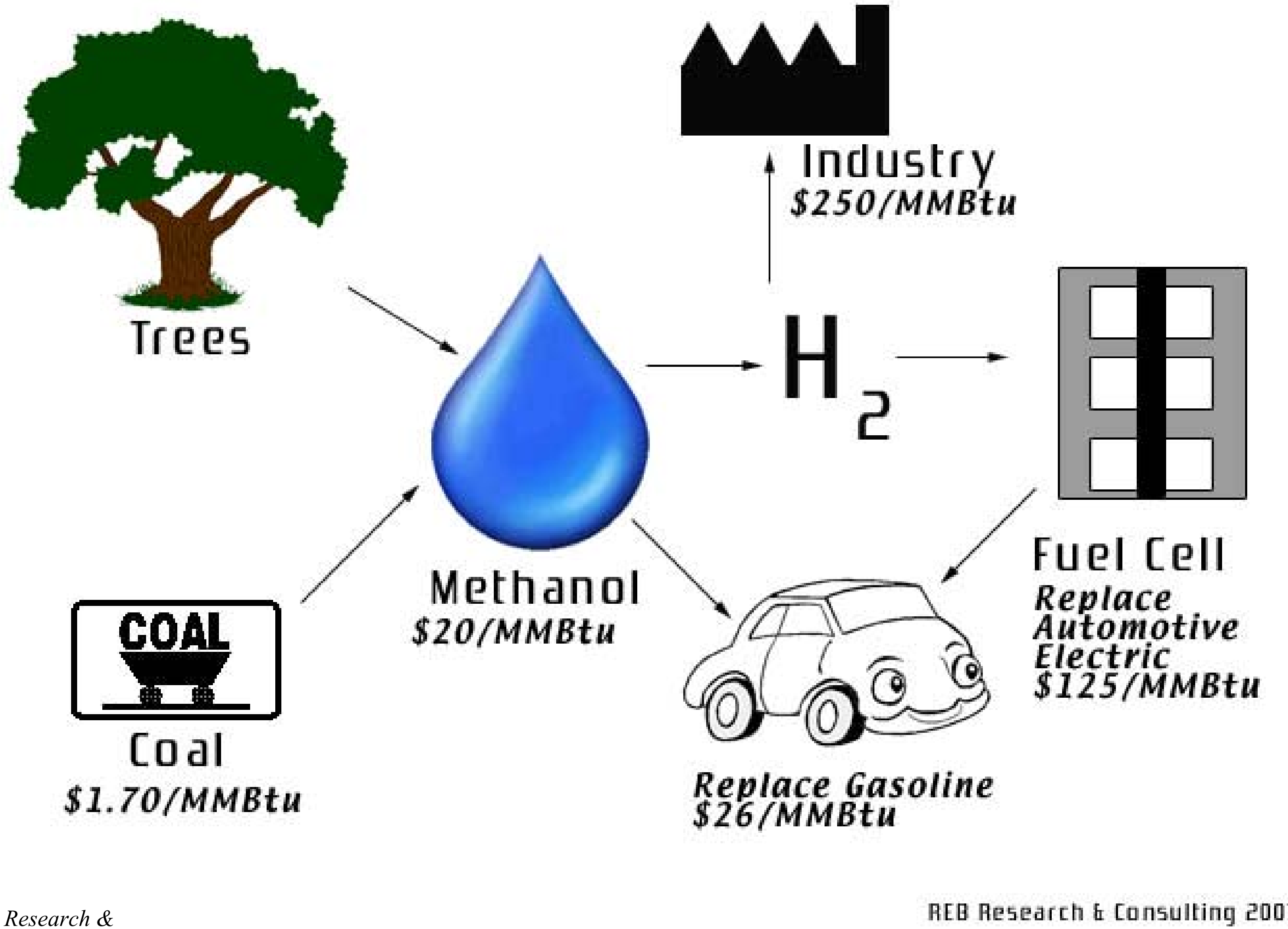
Thank you for your support!

NETL permeation setup

REB's View of Hydrogen and the Energy Picture



Comparison of Metals, Intermetallics and Ceramics

Metals	Intermetallic Compounds	Ceramics
high densities	Intermediate densities	low densities
intermediate elastic moduli	fairly high elastic moduli	high elastic moduli
extensive ductility@RT	little ductility@RT	no ductility@RT
moderately high tensile and compressive strength @RT	variable tensile strength, fairly high compressive strength @RT	variable tensile strength, high compressive strength @RT
fairly low hot strength	high hot strength	very high hot strength
mediocre/low hot oxidation resistance	fairly high hot oxidation resistance	high hot oxidation resistance
high electrical conductivity	moderately high electrical conductivity	very low electrical conductivity
high RT fracture toughness	low RT fracture toughness	low RT fracture toughness