Membrane reactors for CO_2 capture:
Development of V-based alloys for syngas separation

Michael Dolan and **Daniel Roberts**

6th International Freiberg Conference on IGCC and XtL Technologies
May 19-22, 2014. Radebeul (Dresden), Germany

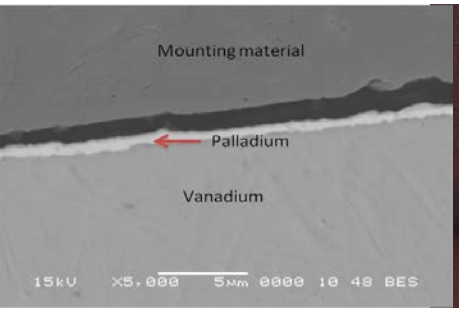
CSIRO ENERGY
www.csiro.au

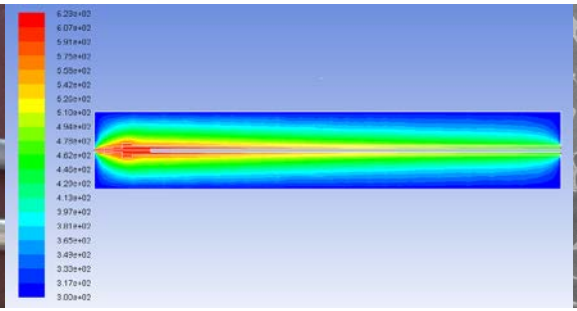
CSIRO

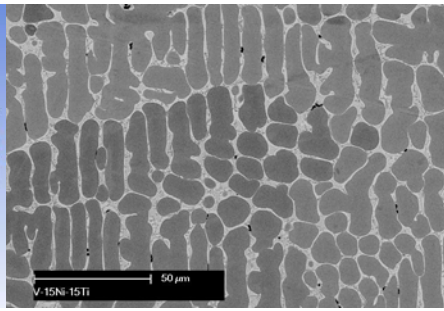
anlecr&d

Capturing CO_2 from coal-based power systems

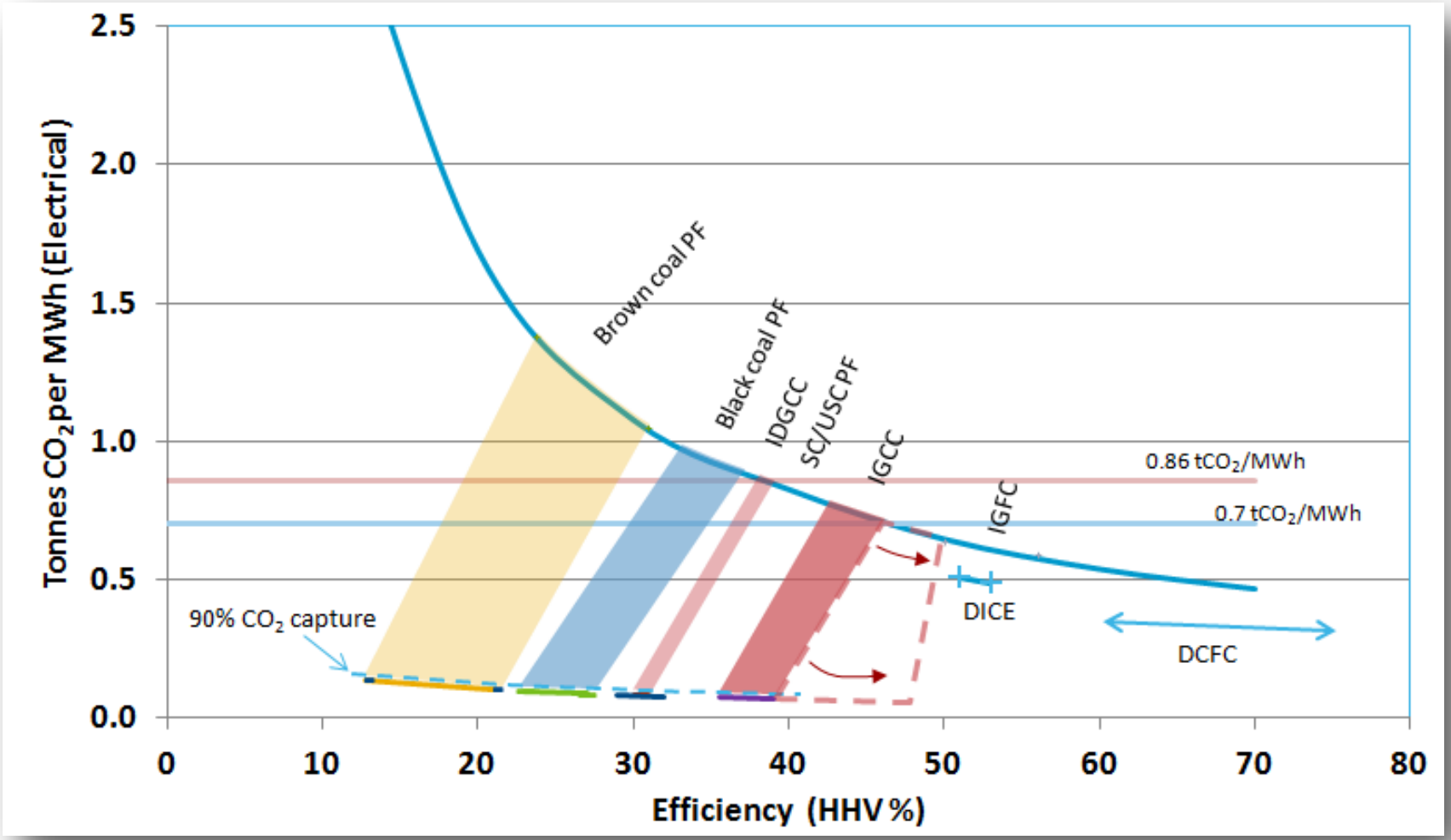
- Post-combustion capture
  - Solvent-based
  - Sorbent-based
- Oxy-fuel combustion
  - Cryogenic distillation
  - Ceramic membranes
  - Chemical looping
- Pre-combustion capture
  - Gasification-specific
  - H_2/CO_2 separation



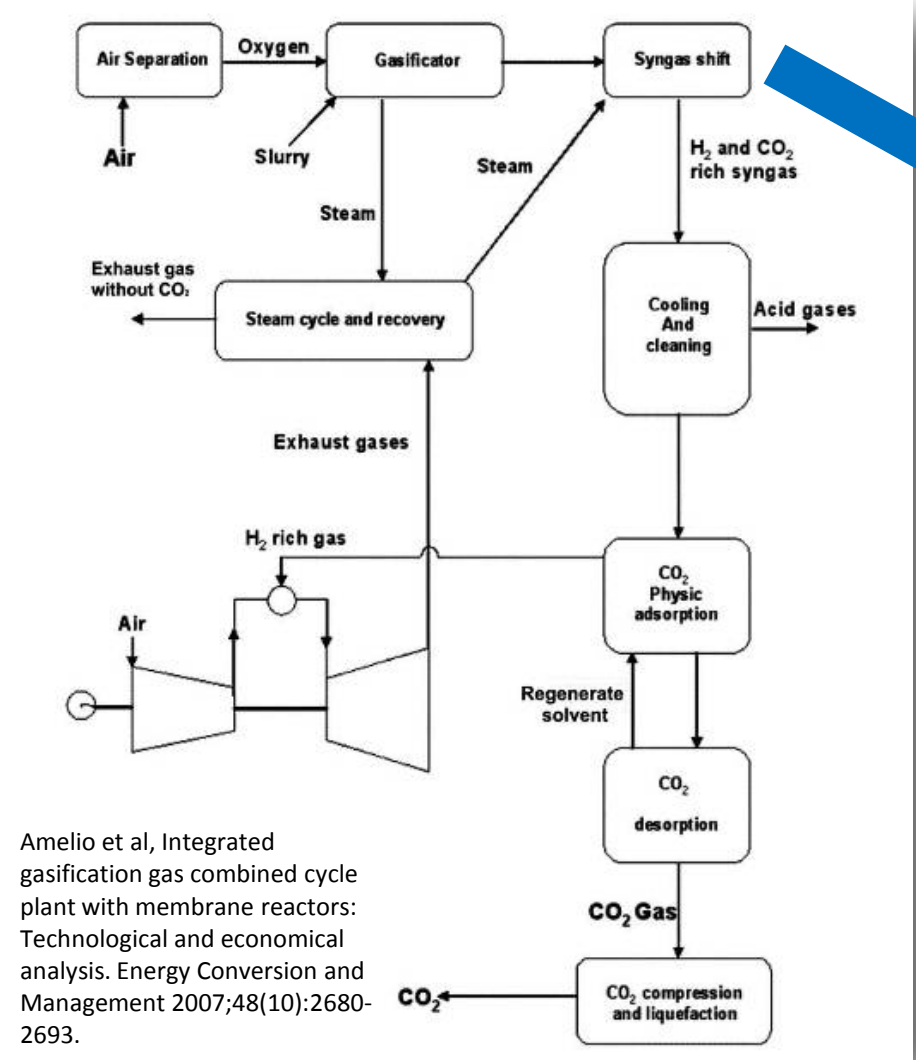




Pre-CC has an inherent efficiency advantage



Pre-combustion CO_2 capture (conventional)



Amelio et al, Integrated gasification gas combined cycle plant with membrane reactors: Technological and economical analysis. Energy Conversion and Management 2007;48(10):2680-2693.

WGS reaction:
$CO + H_2O \rightleftharpoons H_2 + CO_2$
Two stages required (400 & 200 °C) to achieve high conversion

Proven, modular processes

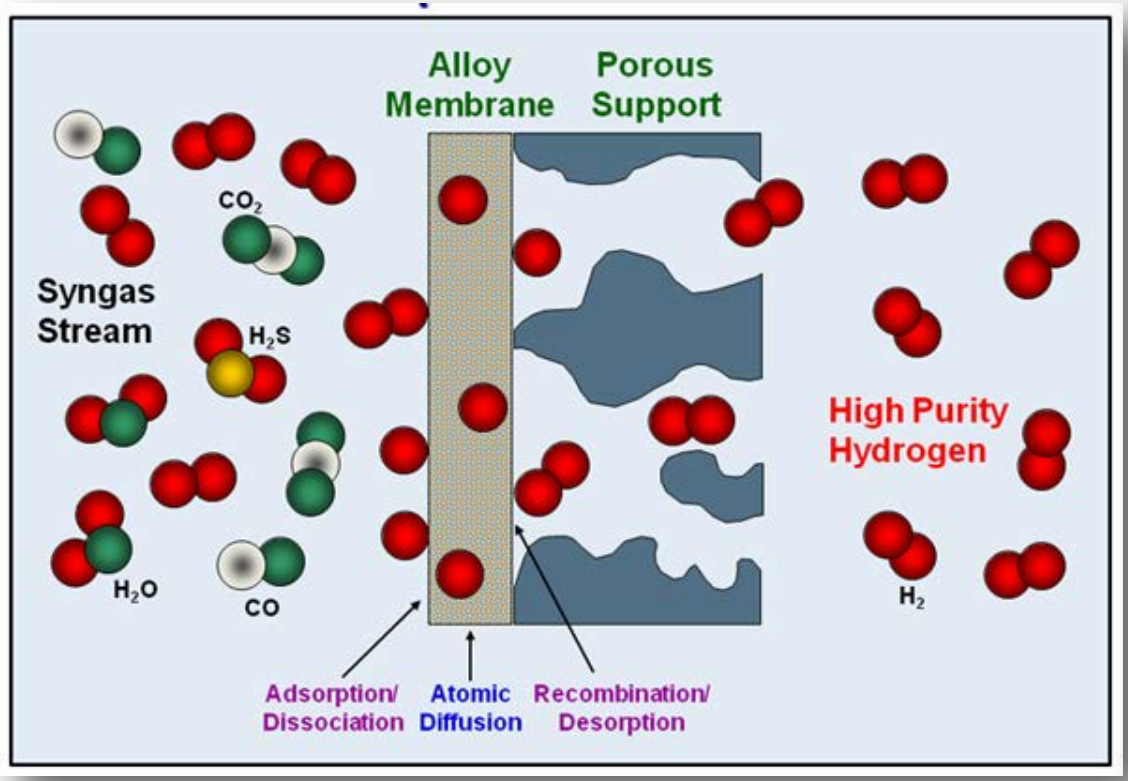
ZeroGen
smarter, cleaner power

CSIRO

WGS catalytic membrane reactor

What is a membrane?

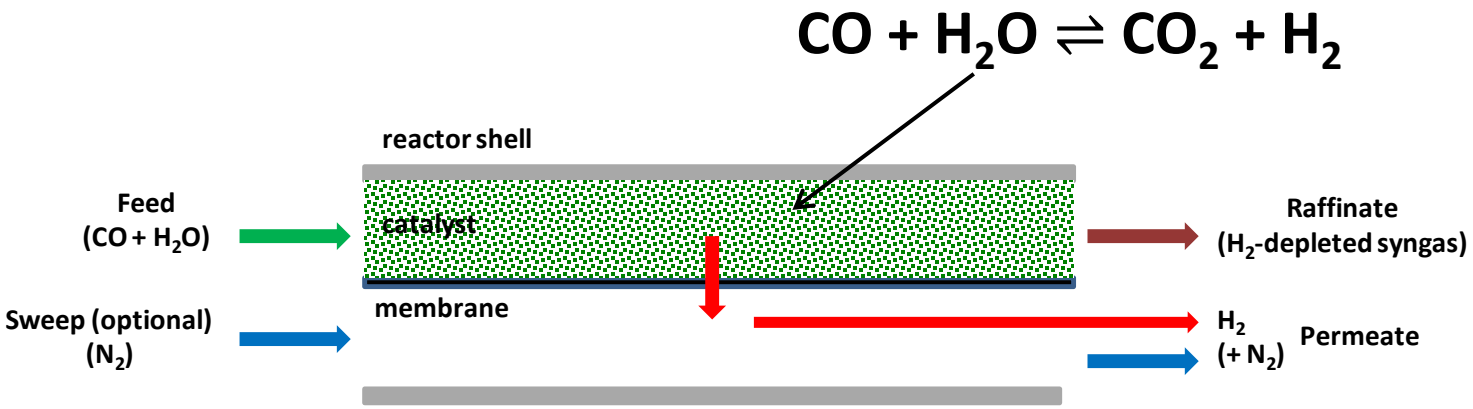
A selectively-permeable 2-D structure



Desirable characteristics

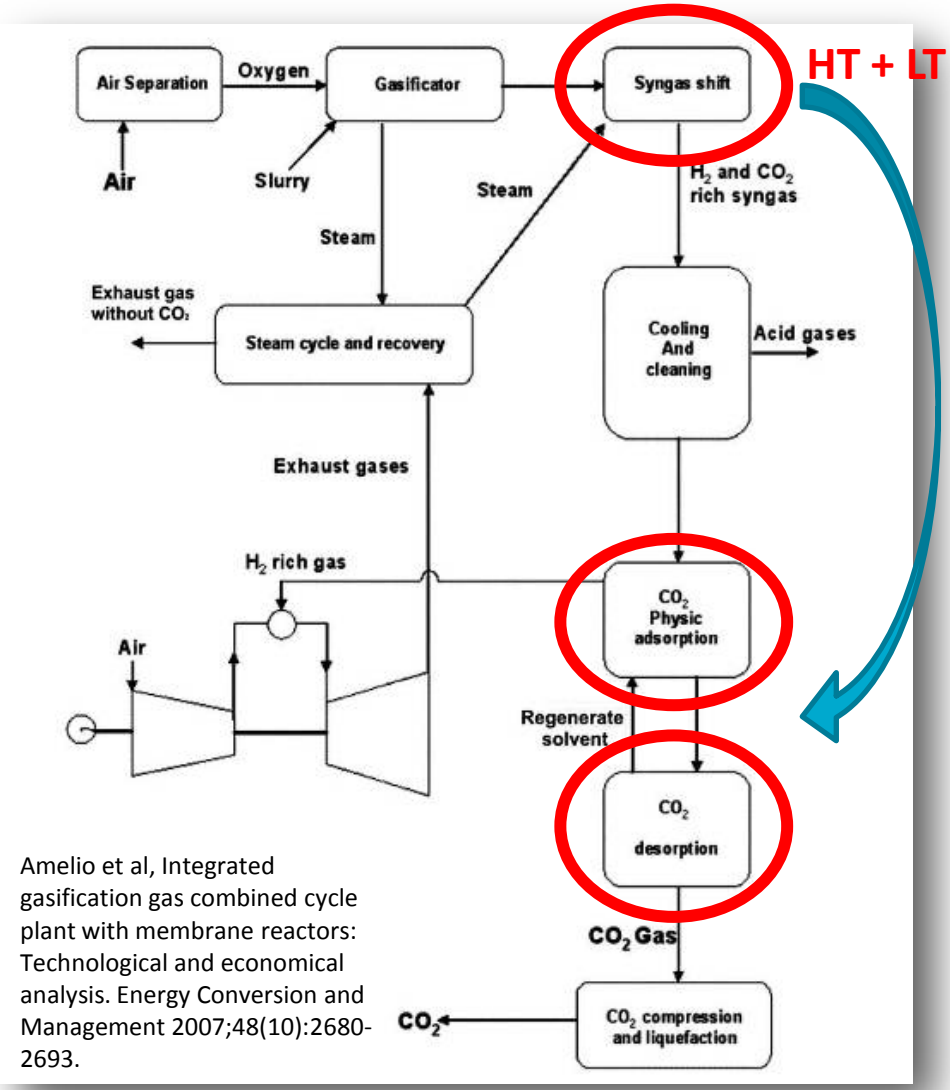
- H_2 throughput
  - 1.0 mol/m^2/s
  - High permeability
  - High trans-membrane pressure
- Cost
  - \$1000/m^2
  - Inexpensive raw materials
  - Simple manufacturing method
- Durability
  - 5 years
- Tolerance to CO and H_2S
  - 50 ppm
- Operating Temperature
  - 400°C for CO shift

The catalytic membrane reactor (CMR)



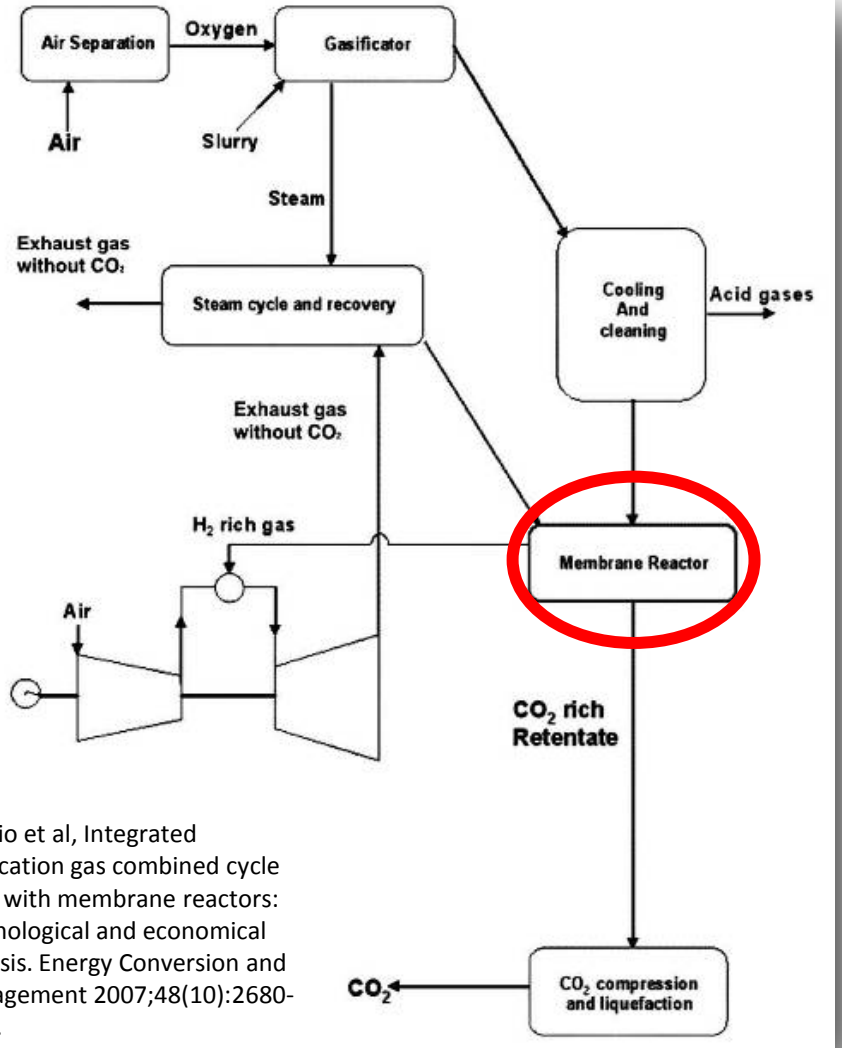
- Overcomes equilibrium barrier
- Process intensification
- Thermal efficiency

Pre-combustion CO_2 capture (conventional)



Amelio et al, Integrated gasification gas combined cycle plant with membrane reactors: Technological and economical analysis. Energy Conversion and Management 2007;48(10):2680-2693.

Pre-combustion CO_2 capture (membrane reactor)



Amelio et al, Integrated gasification gas combined cycle plant with membrane reactors: Technological and economical analysis. Energy Conversion and Management 2007;48(10):2680-2693.

500 → 600°C

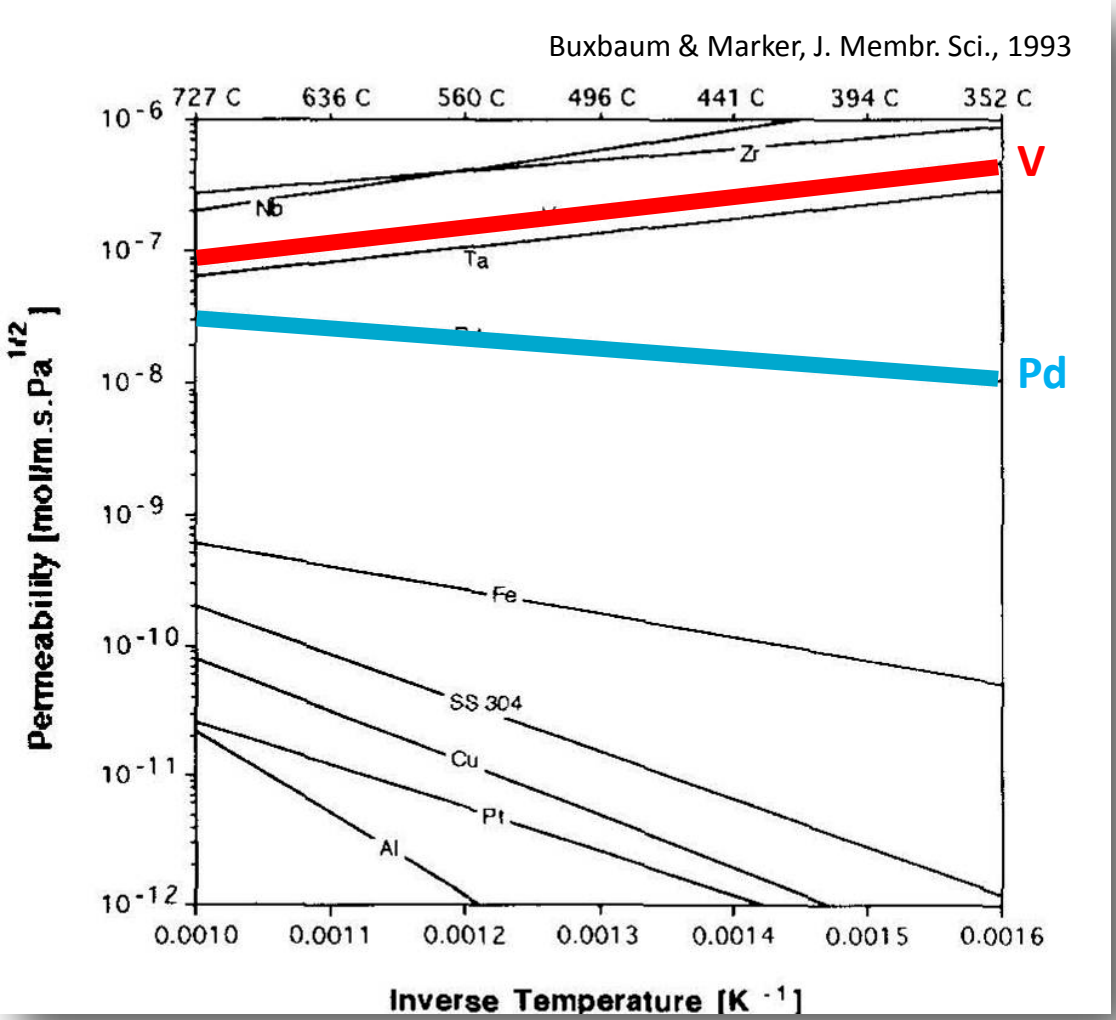
350 → 400°C

Alloy membrane development

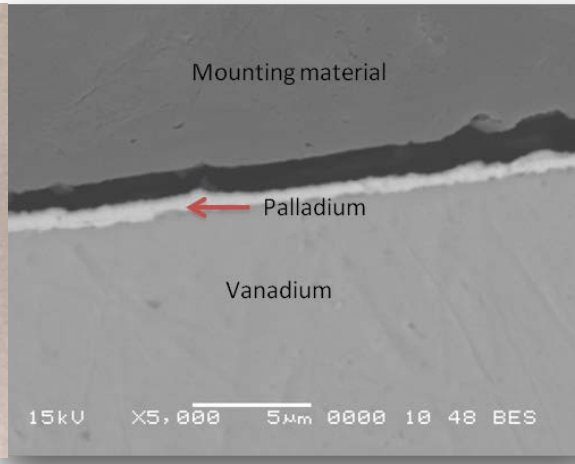
Hydrogen permeability of metals

- Palladium
  - $20,000/kg
  - $US 350 per m^2 per µm
  - Membranes must be < 5 µm thick

- Group IV and V metals
  - Inherently brittle BUT
  - Highly permeable
    - Membranes can be > 100 µm thick
  - Much cheaper than Pd
    - V: $30/kg (as FeV)
    - Nb: $40/kg (as FeNb)
    - Ta: $350/kg



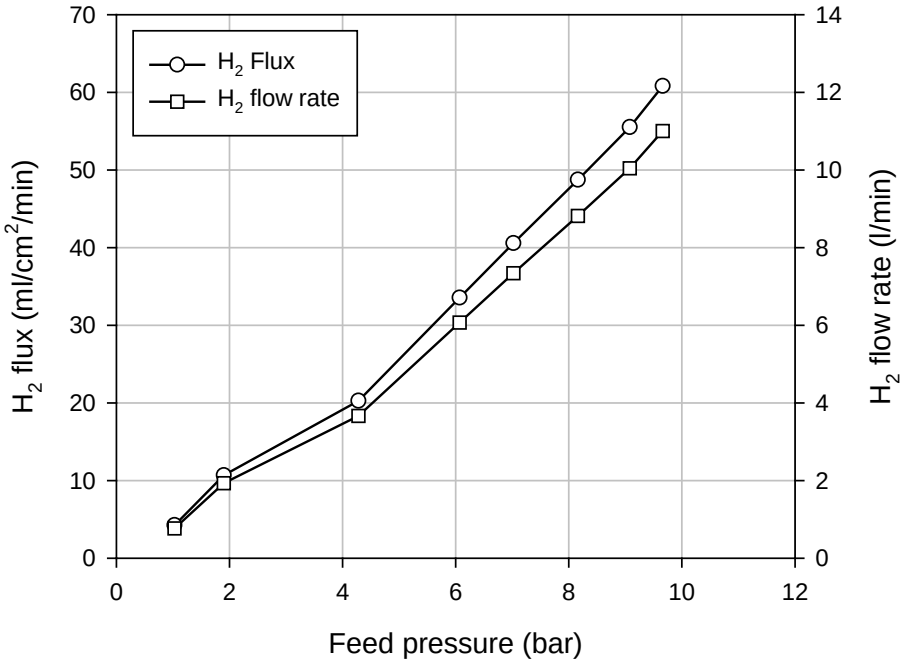
Vanadium-based membranes



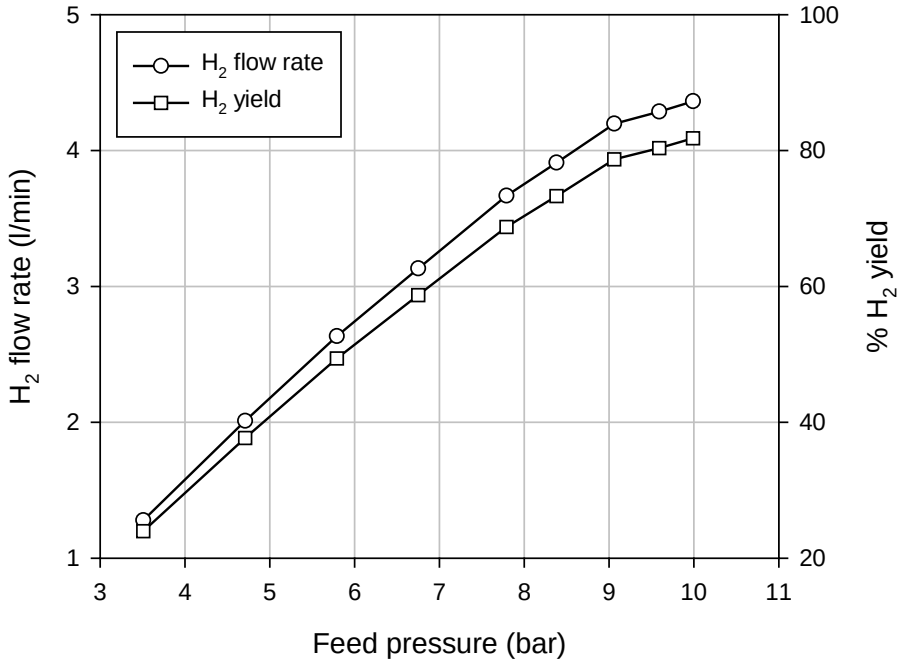
- V-based alloy tube (alloyed for embrittlement resistance)
- Diameter: 3/8” OD
- Wall thickness: currently 0.2 mm, heading for 0.1 mm (flux ↑)
- Length: currently 33 cm, heading for 100 cm
- Self-supporting ($\Delta P > 20$ bar) and stable at 400°C
- Surface catalysts:
  - feed side: S-tolerant alloy (electro- or electroless plated Pd-Au or Pd-Cu)
  - permeate side: Pd (or Ni?)

Vanadium-based membranes

180 cm^2 module at 400°C



Pure H_2 feed



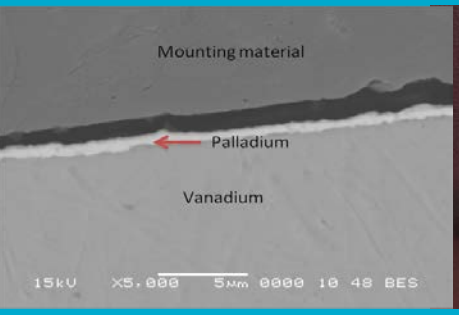
Shifted syngas feed

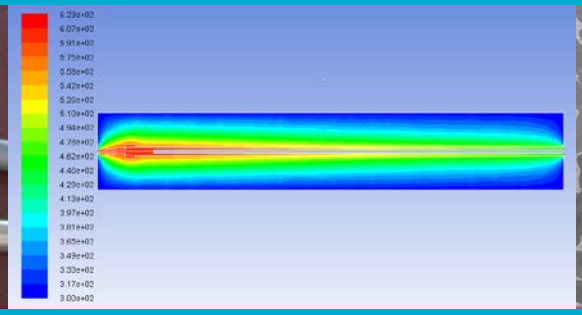
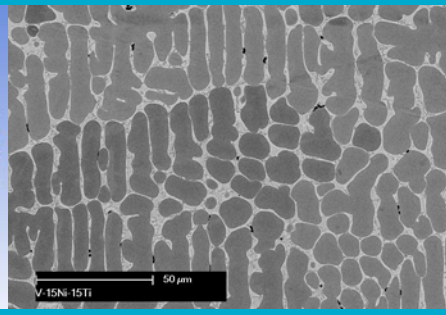
33% H_2 + 22% CO_2 + 44% H_2O, 16 L/min

Summary

Summary

- Pre-combustion CO_2 capture: inherent efficiency advantage over PCC
- Membrane reactor: process intensification, greater efficiency than stand-alone shift and separation stages
- Membranes: Pd consumption must be minimised
  - Self-supporting V-based are a low-cost alternative
- Future work:
  - Optimisation of dissociation catalyst coating (S-tolerance and Pd minimisation)
  - Slipstream testing (exposure to realistic syngas)
  - Scale-up
    - $0.01m^2$ (currently) to $1m^2$ membrane modules.



Energy Technology
Michael Dolan
Research Team Leader

t +61 7 3327 4126
e michael.dolan@csiro.au
w www.csiro.au/energy