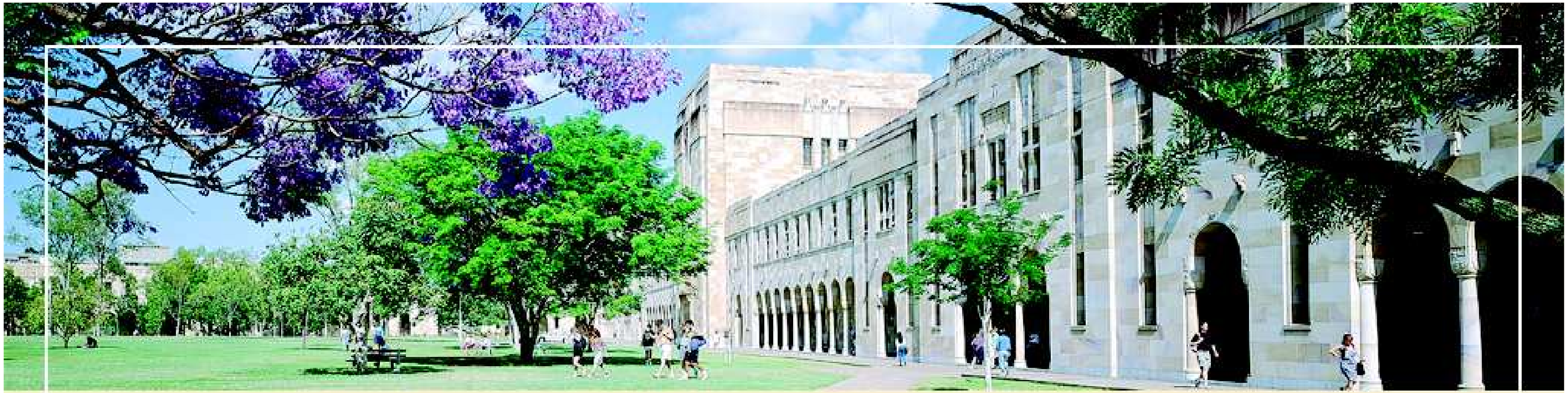


Hydrogen Production

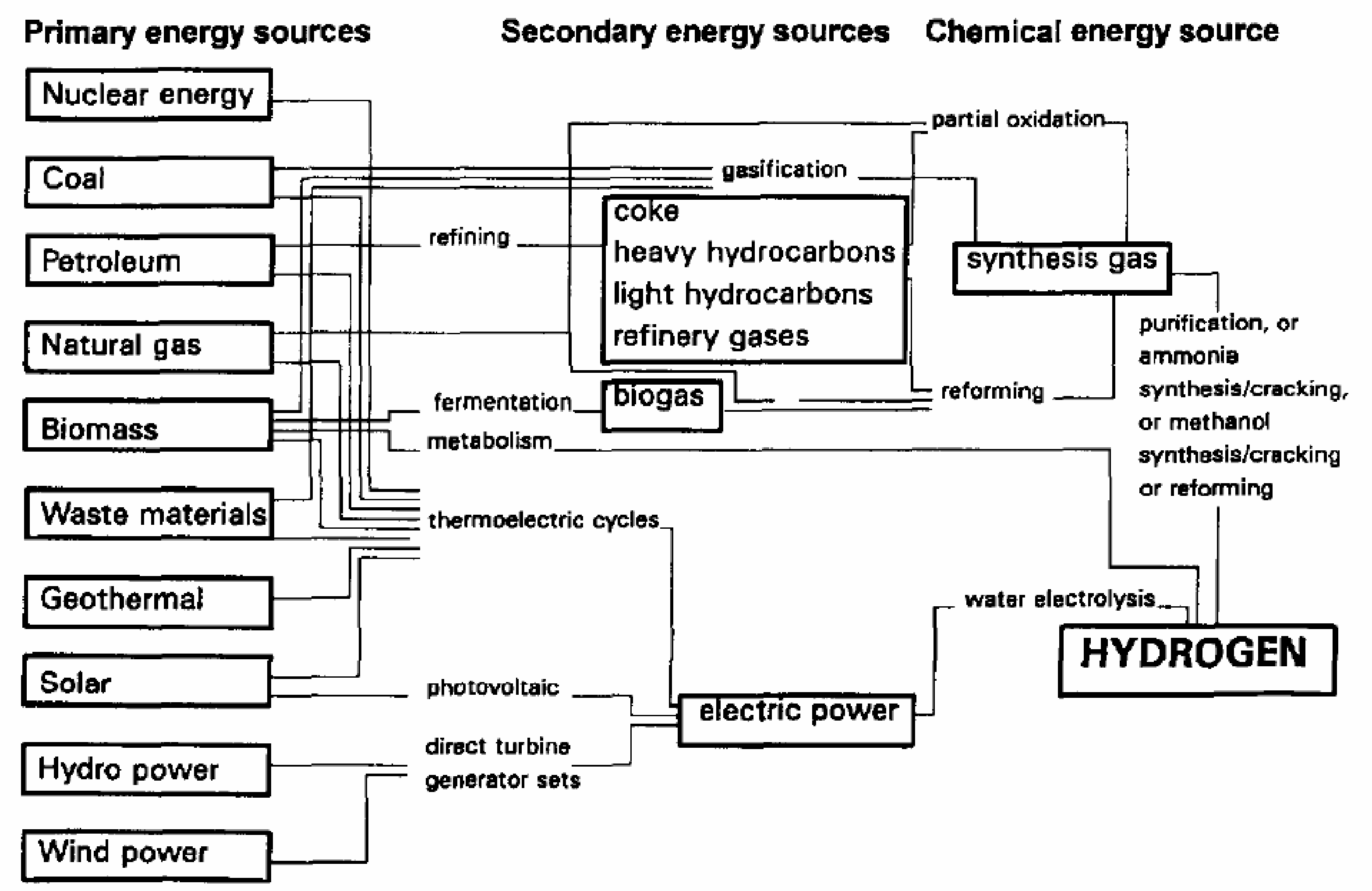
Andrew Dicks

School of Engineering
The University of Queensland

Neutrons for the Hydrogen Economy
ANSTO
22 June 2007

THE UNIVERSITY OF QUEENSLAND
AUSTRALIA

Production of hydrogen



THE UNIVERSITY OF QUEENSLAND AUSTRALIA

Summary

- Hydrogen from water
  - Electrolysis
  - Photocatalysis
  - Biological catalysis
  - Thermal decomposition
  - Chemical cycles
- Hydrogen from hydrocarbons
  - Anaerobic pyrolysis/thermal cracking
  - Gasification
  - Steam reforming

Hydrogen from water

Electrolysis – redox reaction

- Water is oxidized at the anode.

  $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

- Water is reduced at the cathode.

  $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

Most recent commercial electrolysers use a PEM membrane (formerly alkali cells), low current density means higher efficiency but at higher cost. Efficiencies of 60—70% are routinely achieved at reasonable cost. DOE target for 2010 is 75%. New low-cost nanomaterials electrodes by Quantum Sphere have achieved 75% at 300 mA/cm2.

Hydrogen from water

Photocatalysis

Fujishima & Honda 1972

Titania (anatase) is the most widely studied semiconductor because it is inert, stable, and has redox potential is within its bandgap range:

Electronic absorption edge occurs in the UV (3.2 eV or 400 nm).

Many studies seek to improve band gap by doping (e.g. with oxides or but efficiency remains low (below 10%) and there are many materials inconsistencies

UNSW have characterised TiO_2 finding defects (Ti and O vacancies), and believe materials can be improved by tailoring the defect properties

ANSTO looking at functionalising the surface of TiO_2

…..

Hydrogen from water

Photocatalysis

Other materials can be used:

- ZnO (E_g 3.2 eV)
- ZnS (E_g 3.6 eV)
- Fe_2O_3 (E_g 3.1 eV)
- WO_3 (E_g 2.8 eV)
- $SiTiO_3$ (E_g 3.2 eV)

New materials needed – mesoporous transition metal oxides, composites with nano-crystalline semiconductors within the pores of host structures, that can be further modified through ion implantation

Hydrogen from water

Biological catalysis of water splitting by enzymes

A three step process:

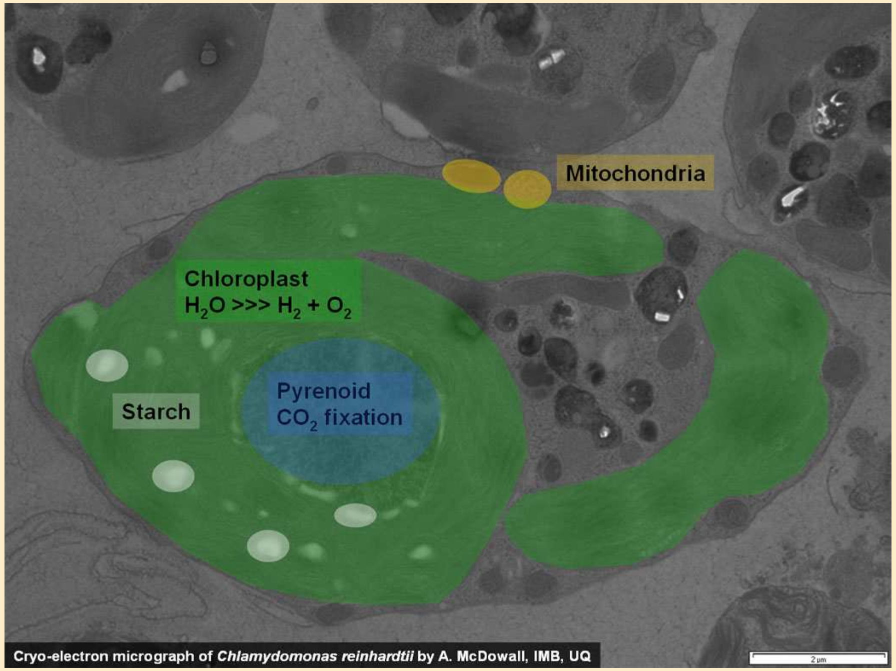
1. Photosystem II

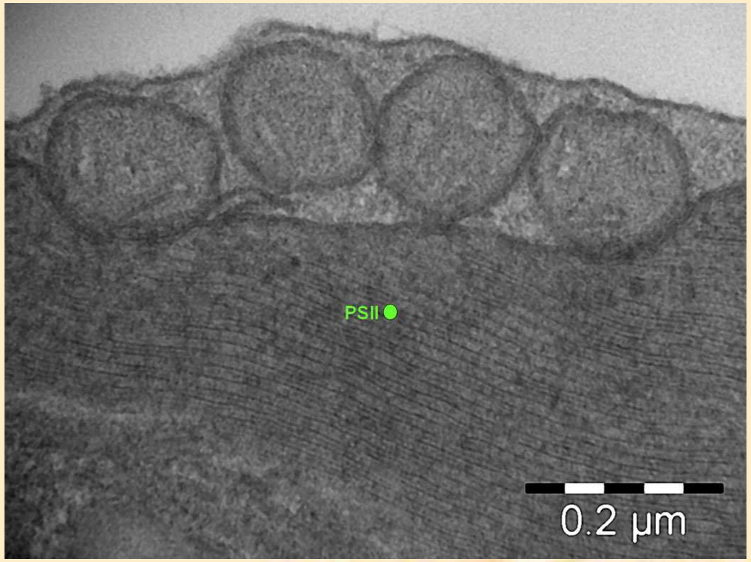
   $2H_2O = 4H^+ + 4e^- + O_2$ (aerobic phase, atmospheric oxygen)

2. $H^+ + e^-$ is stored by reaction with CO_2 as starch through photosynthesis
3. Starch is decomposed by hydrogenase to hydrogen under anaerobic conditions

Present work is on modification of green algae, e.g. *Chlamydomonas*

Hydrogen from water





Hydrogen from water

Thermal decomposition

Above about 1800 K, water (steam) begins to dissociate into a mixture of H2, O2, H2O, O, H and OH. The extent of dissociation increases with increasing temperature and decreasing pressure. The water and the diatomic hydrogen and oxygen species completely dissociate into atomic H and O above about 3500 K under equilibrium conditions at 1 mm Hg absolute pressure.

Separation of H_2 and O_2 is the main problem in addition to achieving high temperature.

Quenching proposed by CNRS 1986

Use of glow discharge and ceramic dissociator nozzle investigated by Pyle et al 1998

So far only low efficiencies (up to 2%) have been achieved

Hydrogen from water

Water-splitting using chemical cycles

Sulphur-iodine cycle

$2H_2SO_4$ +heat at 850℃ $\rightarrow$ $2H_2O + 2SO_2 + O_2$
$4H_2O + 2SO_2 + 2I_2 \rightarrow 2H_2SO_4 + 4HI$
4HI + heat at 300℃ $\rightarrow$ $2I_2 + 2H_2$

Presents engineering challenges

Metal/metal oxide cycle, e.g. at 1900℃

2ZnO + heat $\rightarrow$ 2Zn + O_2

2Zn + $2H_2O \rightarrow$ 2ZnO + $2H_2$

Challenge is to find stable materials that operate at lower temperatures

Hydrogen from hydrocarbons

Pyrolysis, Partial oxidation, or chemical processing:
Steam reforming, cat. cracking, POX, CPO

Natural gases (CH_4)

Bio-gases

Alcohols

Petroleum

Wood

Coal

Gasification with air or oxygen, or pyrolysis

Hydrogen from hydrocarbons

Pyrolysis

$$CH_4 \;=\; 2H_2 + C$$

In principle a simple process but a major engineering challenge – high temperature and C removal.

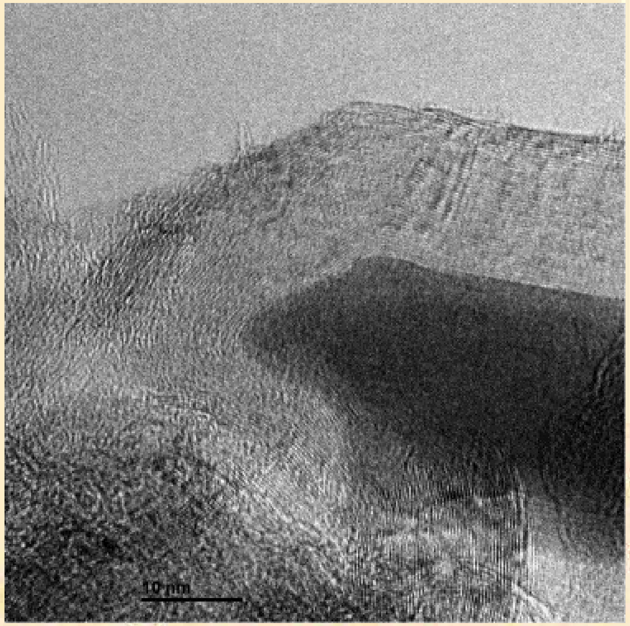
Kaverner CB&H process uses a plasma torch to pyrolyse feed. Plasma gas is recirculated H_2. Process commercial since 1999.

Cost of CB&H process is comparable with steam reforming without CO_2 capture and sequestration

Catalysts required to reduce temp.

Carbon encapsulates catalyst particles

Decomposition of higher hydrocarbons yields secondary products



TEM of Fe (10 wt.%)/AC-lignite
after CH4 pyrolysis in absence of O2
N Murador et al *Catalysis Today*, 116(3), 281

Hydrogen from hydrocarbons

Gasification

A wide variety of processes for heavy liquid petroleum feeds through to coal and biomass

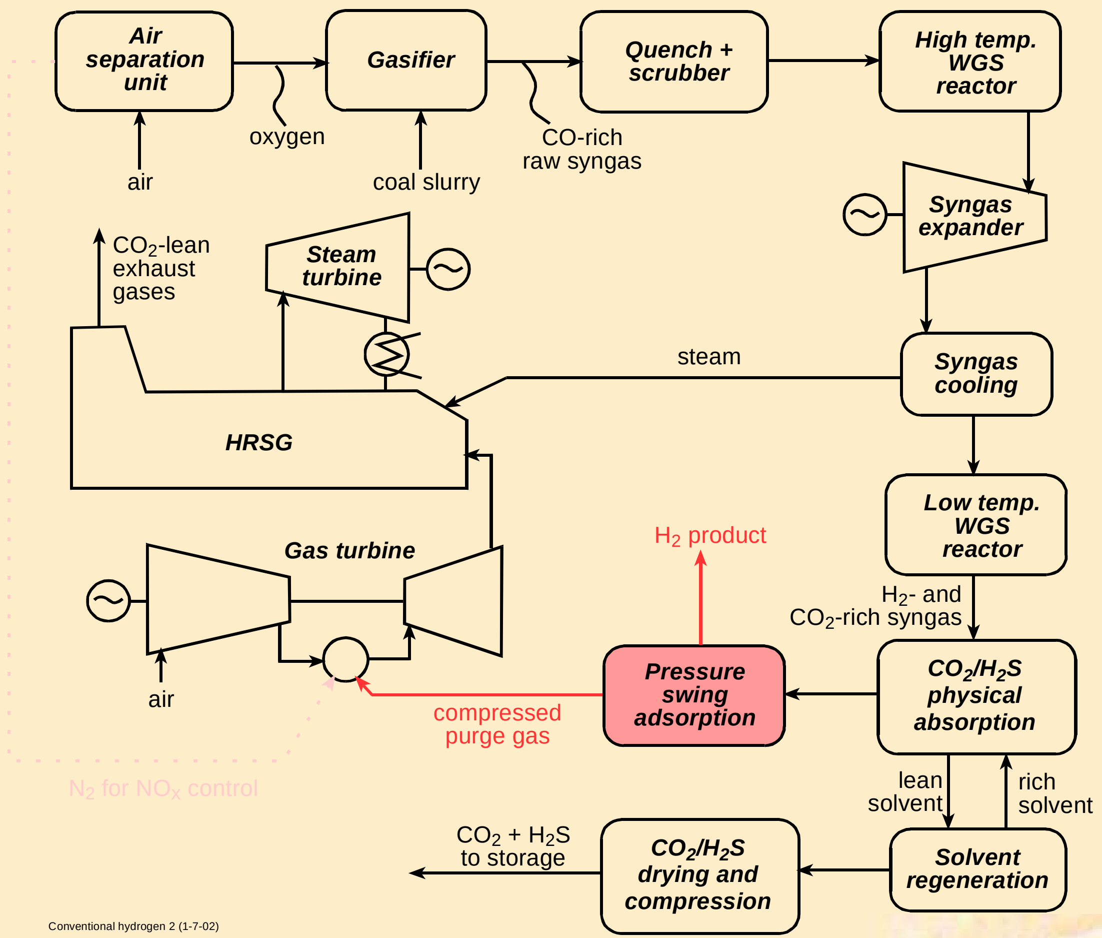
Oxygen-blown or air-blown gasifiers

Fluid bed, entrained bed, or moving bed reactors can be used

Downstream processing required to purify the H_2 and capture CO_2

Products depend on operating conditions and feedstock

Conventional Gasification Technology for H_2 Production with CO_2 Capture



Hydrogen from hydrocarbons

Coal gasifier product gases

	BG-Lurgi gasifier (non-slagging)	BG-Lurgi slagging gasifier	Moving bed O_2-blown (Lurgi)	Fluidised bed (Winkler)	Entrained bed O_2 blown (Texaco)	Entrained bed air-blown	Entrained bed O_2 blown (Shell)
Coal	Pittsburg 8	Pittsburg 8	Illinois no.6	Texas	Illinois no.6	Illinois	Illinois no.6
Ar	trace	Trace	trace	Lignite	0.9	no.6	1.1
CH_4	8.5	7.2	3.3	0.7	0.1	trace	26.7
C_2H_6	0.7	0.1	0.1	4.6	30.3	1.0	63.1
C_2-H_4	0.3	0.2	0.2	28.3	39.6	9.0	1.5
H_2	29.1	39.0	21.0	33.1	10.8	16	4.1
CO	18.0	55.5	5.8	15.5	0.7	6	2.0
CO_2	31.1	3.9	11.8	0.6	0.1	62	1.3
N_2	2.4	4.0	0.2	0.1	16.5	5.0	100.0
NH_4	100.0	100.0	0.4	16.8	1.0	100.0	
H_2O			61.8	0.2	100.0		
H_2S			0.5	100.0			
Total			100.0				

From: Larminie and Dicks, *Fuel Cell Systems Explained*, Wiley 2004

Hydrogen from hydrocarbons

Catalytic steam reforming

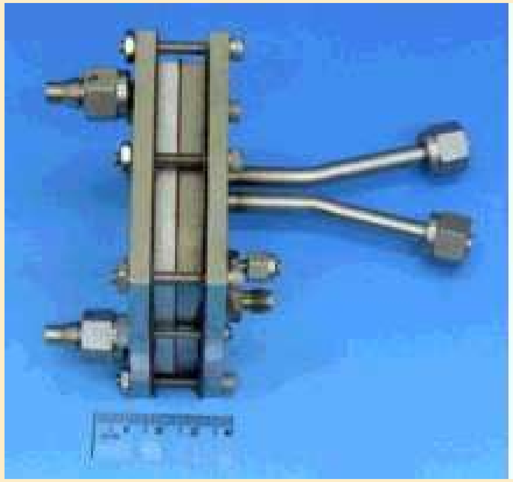
Steam Reforming $CH_4 + H_2O \Leftrightarrow CO + 3H_2$ $\Delta H = +205.9$ *kJ/mol* [1]

(higher hydrocarbons generally react at lower temperatures and are less endothermic)

Water Gas Shift $CO + H_2O \Leftrightarrow CO_2 + H_2$ $\Delta H = -41.1$ *kJ/mol* [2]

Hydrogen from hydrocarbons

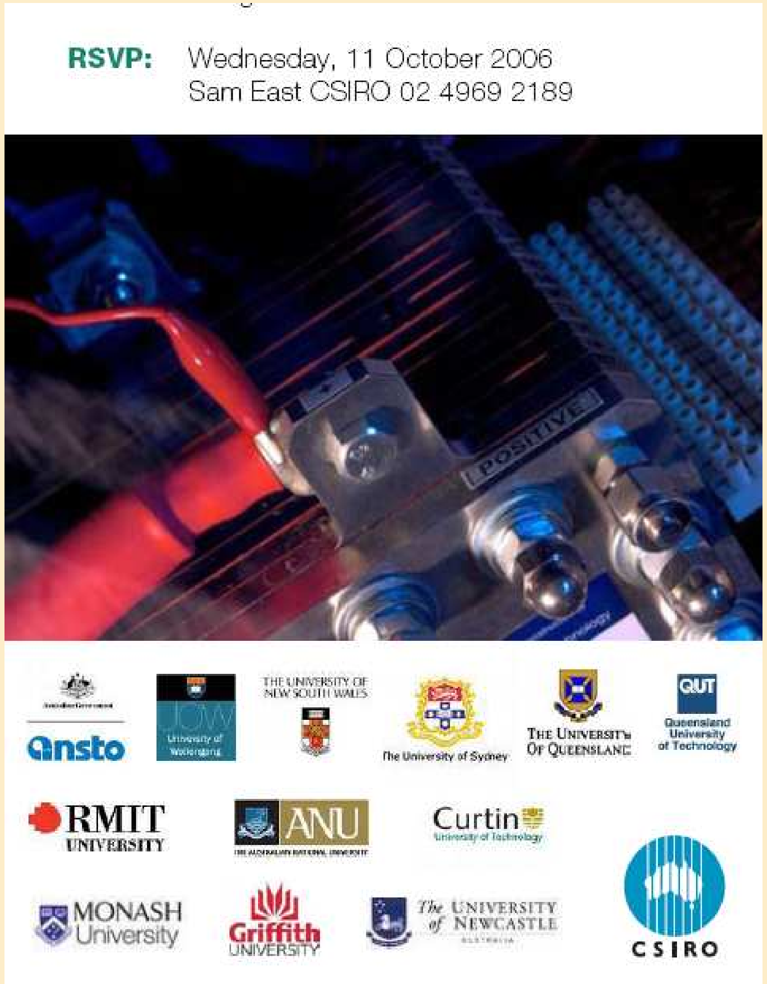
steam reforming at the small scale



Batelle, Northwest National Laboratory Gasoline reformer

Advantica technologies Natural gas reformer

National Hydrogen Materials Alliance



- A cluster of 11 universities and ANSTO
- Budget ca. $10 million 2005-8
- R&D devoted to materials development
  - Production
  - Storage
  - Utilisation (fuel cells)

NATIONAL RESEARCH FLAGSHIPS

CSIRO

Hydrogen Generation and End Use projects:

- *New catalyst materials for hydrogen generation from hydrocarbon fuels*
- *Integration of electrolysis systems*
- *Photocatalytic materials for hydrogen production by water splitting*
- *Materials for advanced hydrogen fuel cells*

Hydrogen Storage projects:

- *Storage materials based on lithium*
- *Storage materials based on magnesium*
- *Storage in carbons*
- *Storage in porous materials*

Supplying Energy To A Changing World

World Hydrogen Energy Conference 2008

Brisbane, Queensland

15 - 19 June 2008