RAL: ISIS & Diamond

ISIS TSII

Oxford

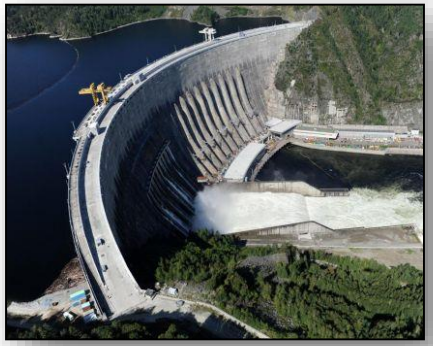
Oxford Chemistry

Session: NH_3 Fuel Use

Facilitator: Bill David

ISIS Facility, Rutherford Appleton Laboratory, UK &
Inorganic Chemistry Laboratory, University of Oxford, UK

ENERGY PRODUCTION


Hydroelectric


Solar

Biomass


Marine


Wind

Gas

WATER

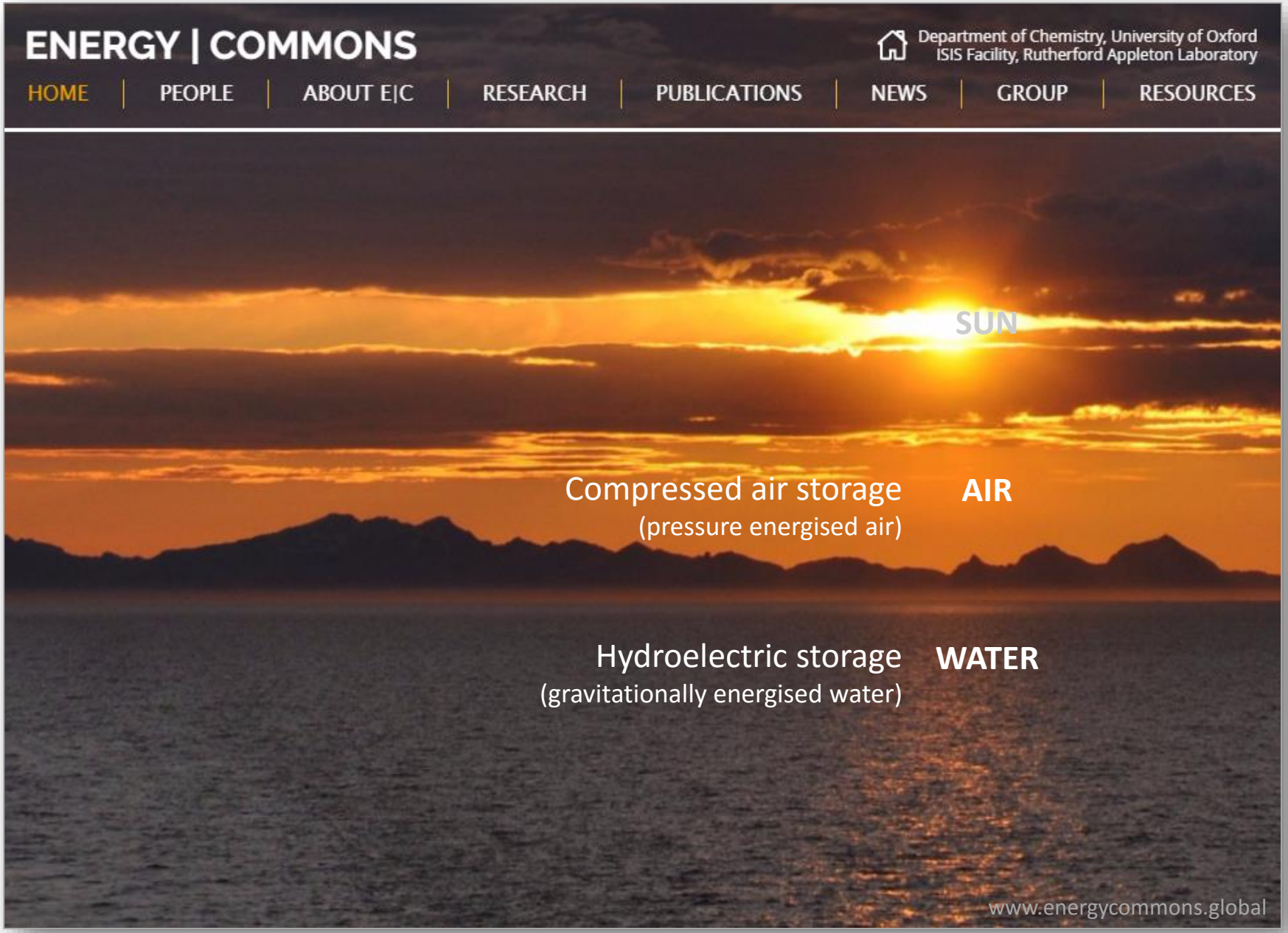

Geothermal


Nuclear


Coal

Can we use the Global Commons to store energy?

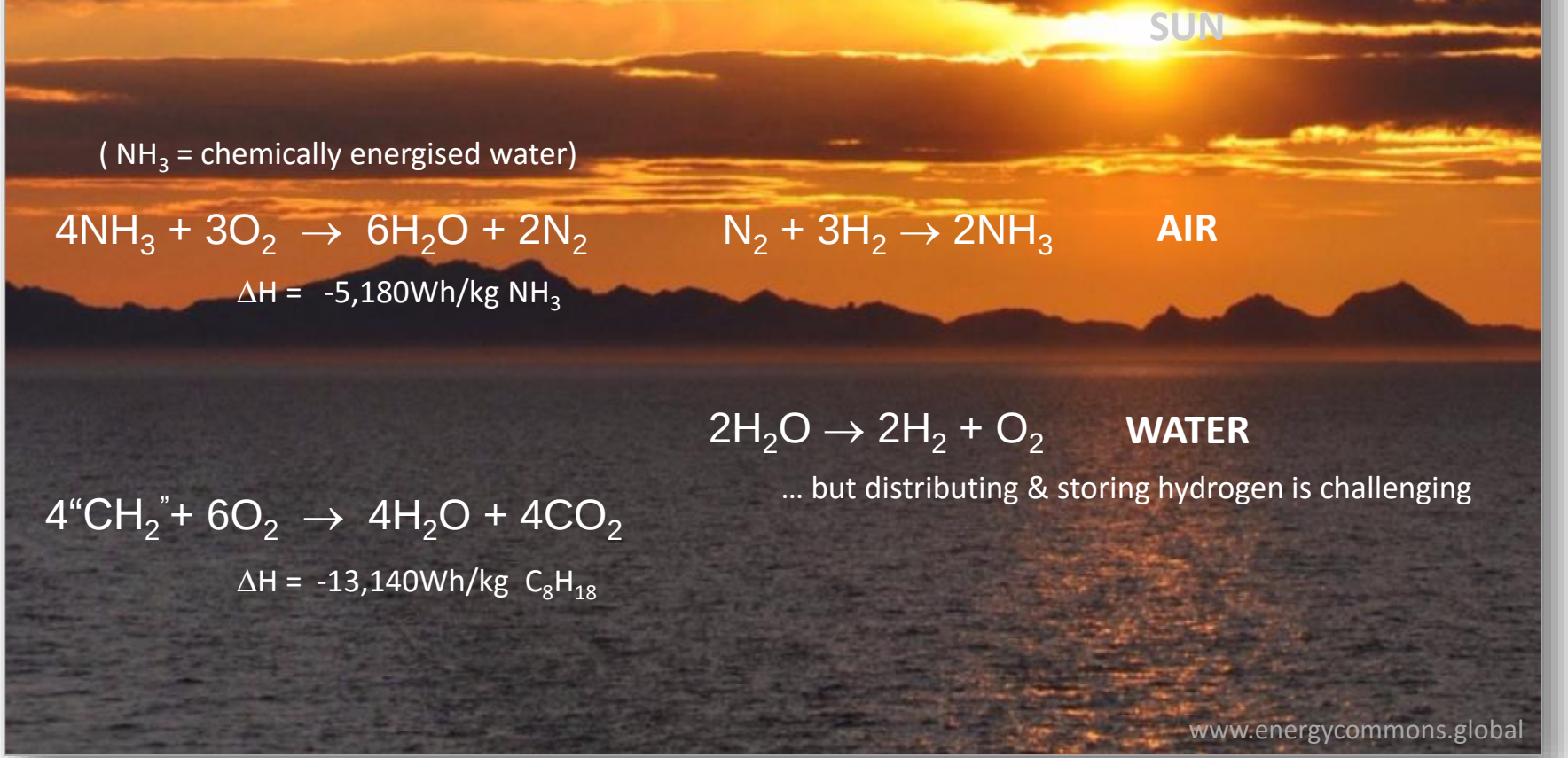
Global Commons


ENERGY | COMMONS
Department of Chemistry, University of Oxford
ISIS Facility, Rutherford Appleton Laboratory
HOME | PEOPLE | ABOUT E|C | RESEARCH | PUBLICATIONS | NEWS | GROUP | RESOURCES
SUN
Compressed air storage
(pressure energised air)
AIR
Hydroelectric storage
(gravitationally energised water)
WATER
www.energycommons.global

Electricity storage

ΔH = -220Wh/kg (Li^+ battery)

… issues with earth abundant materials



(NH_3 = chemically energised water)

$4NH_3 + 3O_2 \rightarrow 6H_2O + 2N_2$ $\quad$ $N_2 + 3H_2 \rightarrow 2NH_3$ **AIR**

ΔH = -5,180Wh/kg NH_3

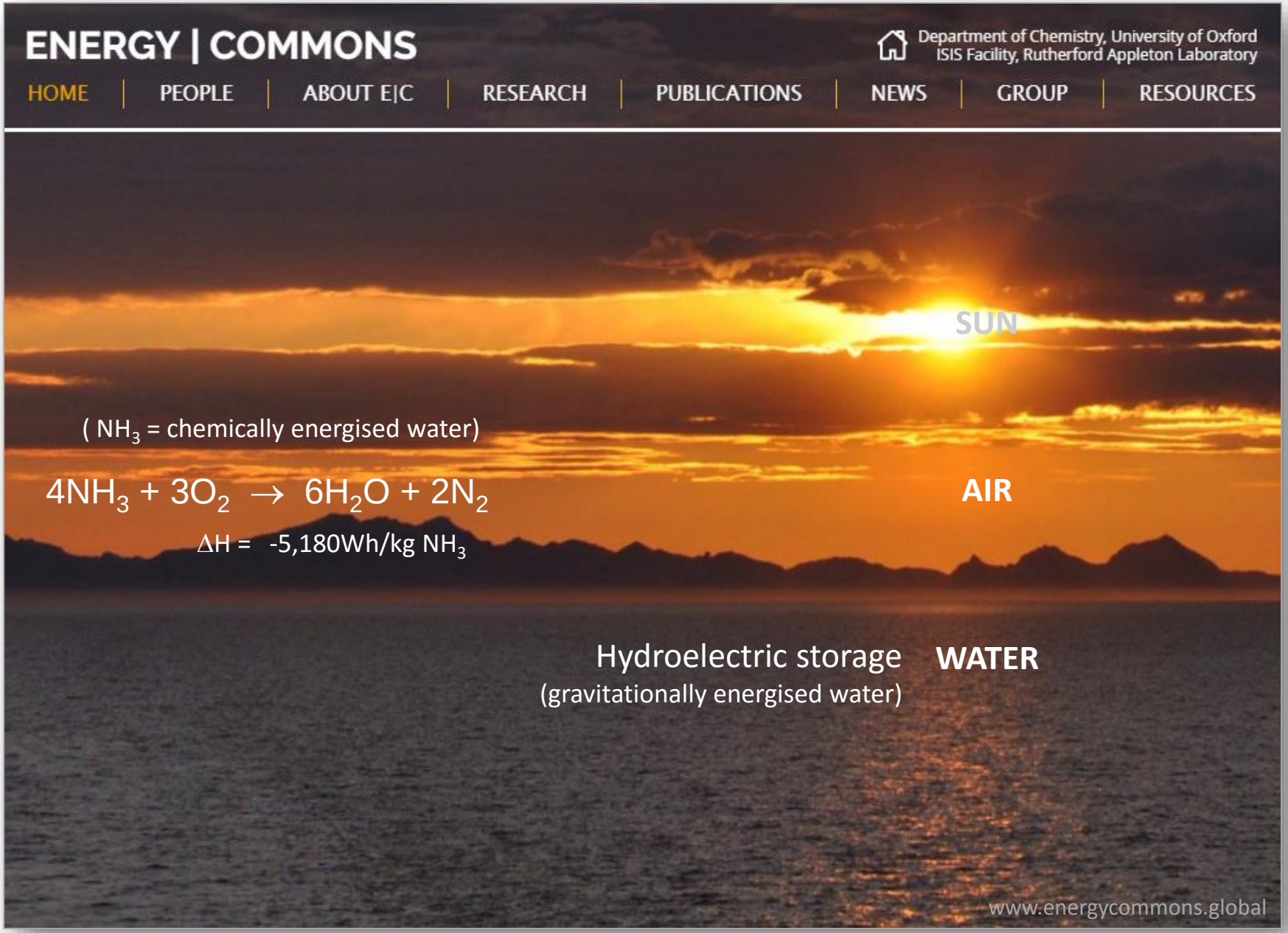
$2H_2O \rightarrow 2H_2 + O_2$ **WATER**

… but distributing & storing hydrogen is challenging

$4\text{“}CH_2\text{”} + 6O_2 \rightarrow 4H_2O + 4CO_2$

ΔH = -13,140Wh/kg C_8H_{18}

www.energycommons.global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SUN
(NH_3 = chemically energised water)
$4NH_3 + 3O_2 \rightarrow 6H_2O + 2N_2$
AIR
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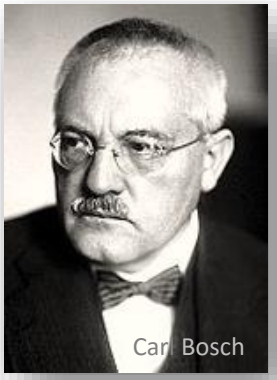
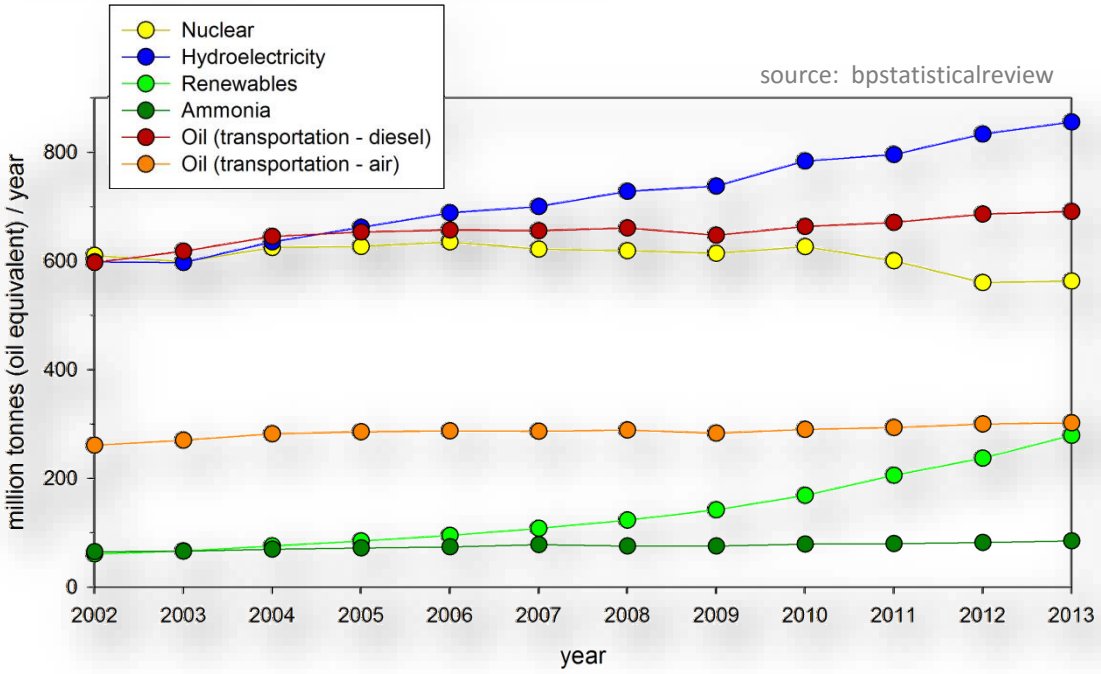
Hydroelectric storage WATER
(gravitationally energised water)
www.energycommons.global

NH_3 | the quintessential non-carbon hydrocarbon



Artificial NH_3 synthesis
The Haber-Bosch process
1909 | 1910



nature International weekly journal of science

Millennium Essay

Nature **400**, 415 (29 July 1999) | doi:10.1038/22672

Detonator of the population explosion

Without ammonia, there would be no inorganic fertilizers, and nearly half the world would go hungry. Of all the century's technological marvels, the Haber-Bosch process has made the most difference to our survival.

- 170 million tonnes / year
- 1% world's energy use
- 2% global CO_2 emissions
- 40% nitrogen in our bodies

PHYSICAL & THERMODYNAMIC PROPERTIES

- 17.6wt% hydrogen
- liquid @ 8bar (298K)
- storage same as butane/propane
- heat of combustion: 5,180Wh/kg
  c.f. (gasoline) 13,140Wh/kg
  (Li^+ battery) ~220Wh/kg

NH_3 Fuel Use : Agenda

1:00 pm	Cracking Ammonia (UK)
1:30 pm	Research and Development of Ammonia-fueled SOFC Systems (Japan)
1:55 pm	Power Generation and Flame Visualization of Micro Gas Turbine Firing Ammonia or Ammonia-Methane Mixture (Japan)
2:20 pm	NO_x Emission Analysis and Flame Stabilization of Ammonia-Hydrogen-Air Premixed Flames (Turkey & USA)
2:45 pm	15 minute break and Refreshments *Nutrition Hub (Lobby)*
3:00 pm	Combustion Characteristics of Ammonia / Air Flames for a Model Swirlburner and an Actual Gas Turbine Combustor (Japan)
3:25 pm	The Raphael Schmuecker Memorial Solar Hydrogen System – an update (USA)
3:50 pm	Development of Ammonia / Natural Gas Dual Fuel Gas Turbine Combustor (Japan)
4:15 pm	Carbon Free Liquid Fuel for Today's (and Tomorrow's) Piston and Turbine Generators (USA)
4:40 pm	Adjourn for the day

RAL: ISIS & Diamond

ISIS TSII

Oxford

Oxford Chemistry

Cracking Ammonia

Bill David[1,2], Josh Makepeace[2], Hazel Hunter[1], Tom Wood[1]

[1]ISIS Facility, Rutherford Appleton Laboratory, UK &
[2]Inorganic Chemistry Laboratory, University of Oxford, UK

cracking

noun [U] • /ˈkræk·ɪŋ/

chemistry **a process in which large molecules of a hydrocarbon are broken down into smaller molecules**

cracking

adjective [U] • /ˈkræk·ɪŋ/

BRITISH *informal* **excellent**

“he is in cracking form to win this race”

“Cracking good cheese, Gromit!”

Katsuhiko Hirose (Toyota)
Head, Fuel cell development

Transport vehicles are now facing again the need to advance to use sustainable fuels such as hydrogen. Hydrogen fuel cell vehicles are being prepared for commercialization in 2015.

Katsuhiko Hirose
"Hydrogen as a fuel for today and tomorrow: expectations for advanced hydrogen storage materials/systems research"
Faraday Discussions, 2011, **151**, 11-18 **DOI:** 10.1039/C1FD00099C

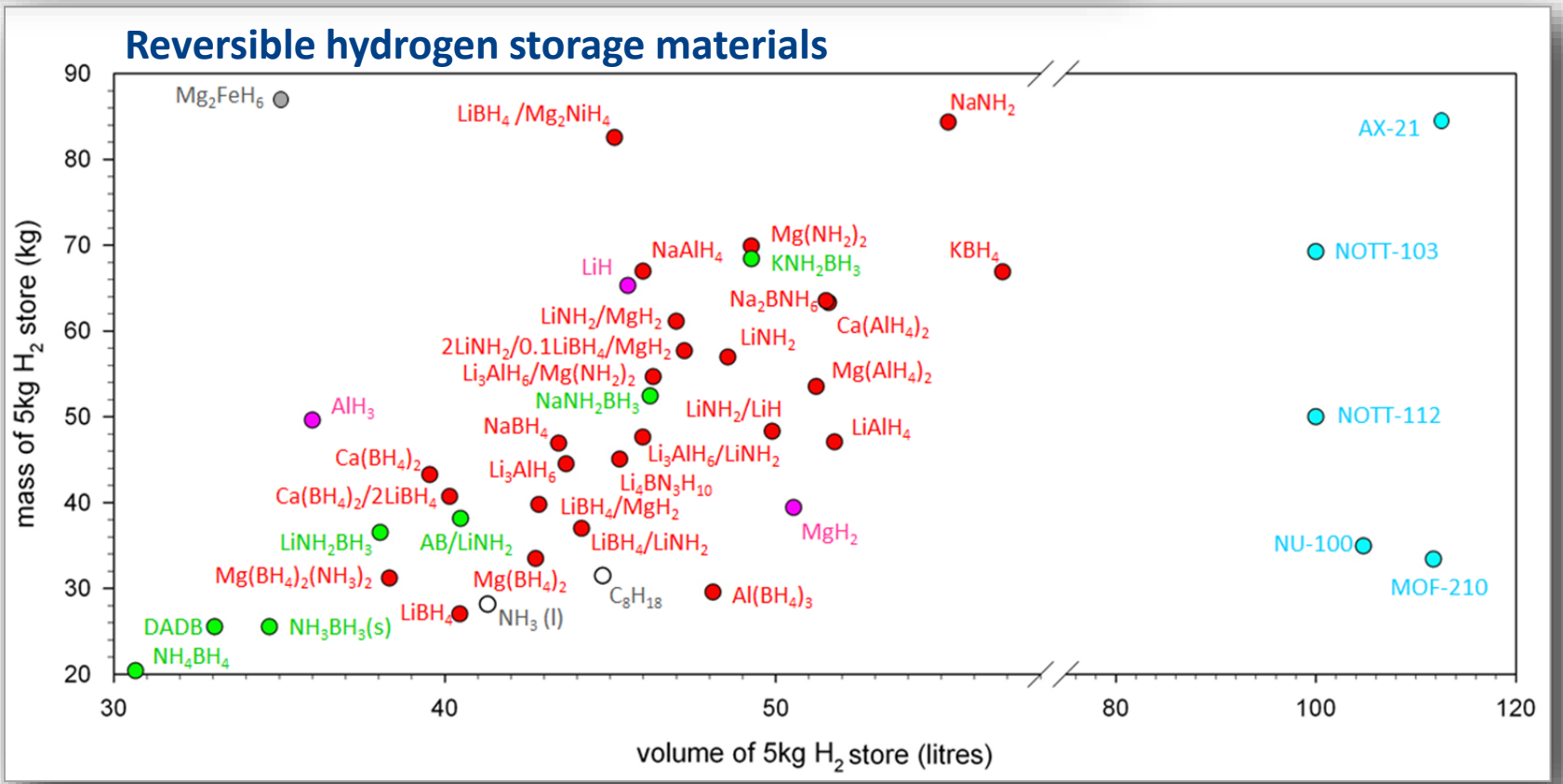
Hydrogen Storage Materials

Faraday Discussion 151

18 - 20 April 2011

Rutherford Appleton Laboratory, Didcot, Oxon, UK

Reversible hydrogen storage materials



… storing hydrogen is a challenge

W I F David,
"Effective hydrogen storage: a strategic chemistry challenge"
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Transport vehicles are now facing again the need to advance to use sustainable fuels such as hydrogen. Hydrogen fuel cell vehicles are being prepared for commercialization in 2015.

Despite intensive research by the world's scientists and engineers and recent advances in our understanding of hydrogen behaviour in materials, the only engineering phase technology which will be available for 2015 is high pressure storage.

Thus industry has decided to implement the high pressure tank storage system.

Katsuhiko Hirose
"Hydrogen as a fuel for today and tomorrow: expectations for advanced hydrogen storage materials/systems research"
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THE HYDROGEN CYCLE

H ABSORPTION

H_2

HYDROGEN STORAGE

700 bar H_2

H DESORPTION

H_2

WATER SPLITTING

H_2

O_2

H_2O

ENERGY IN

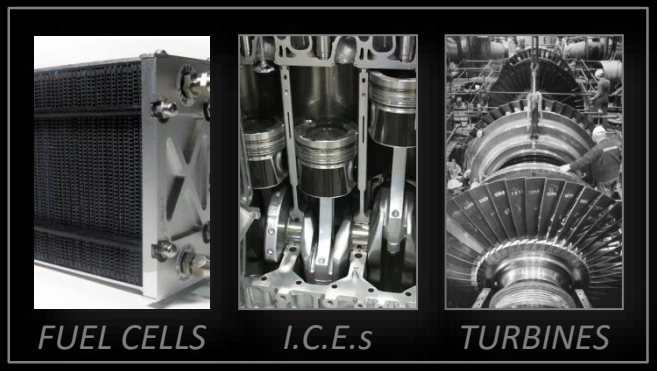
H_2

O_2

H_2O

FUEL CELL COMBUSTION

ENERGY OUT



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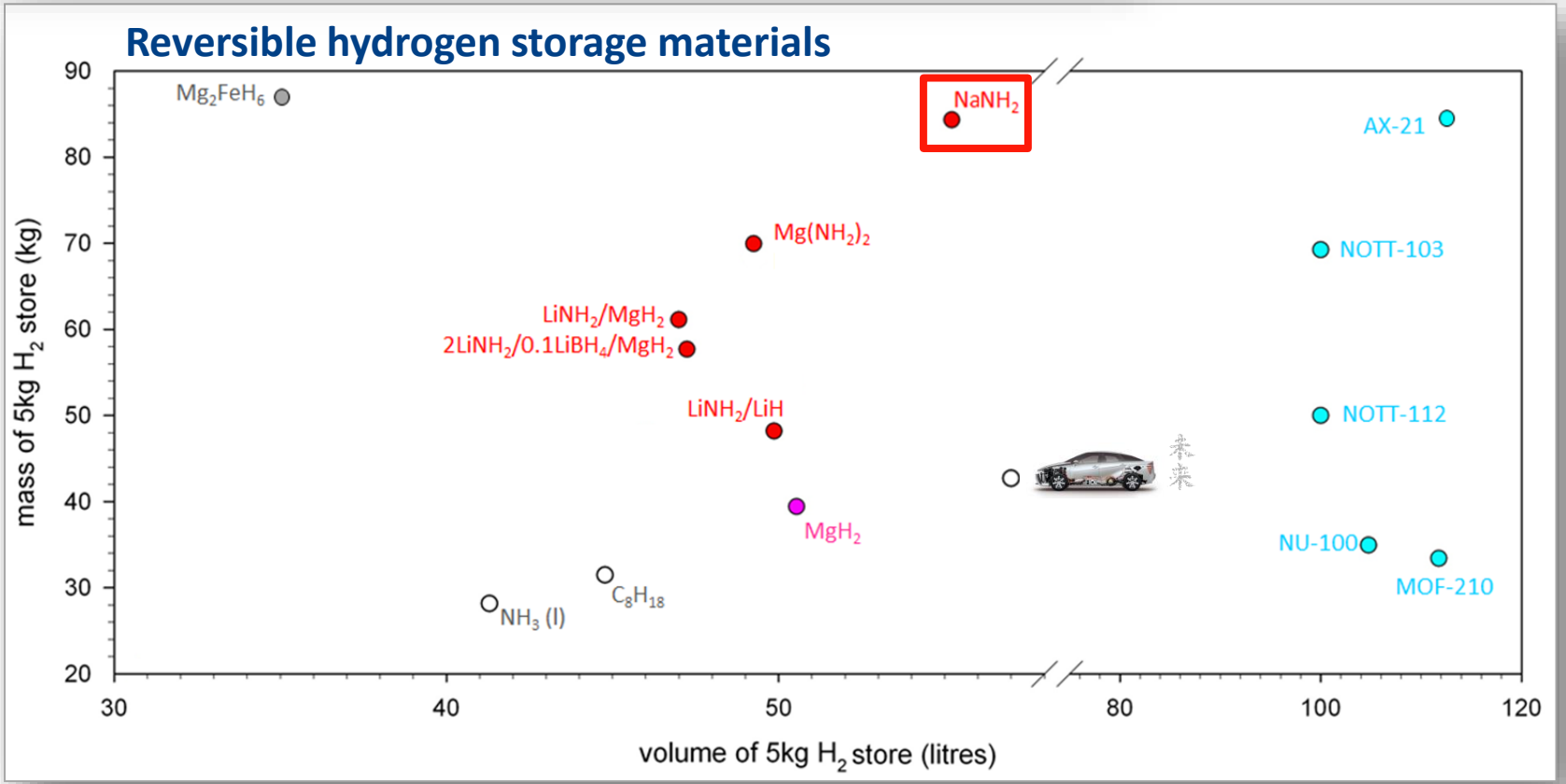

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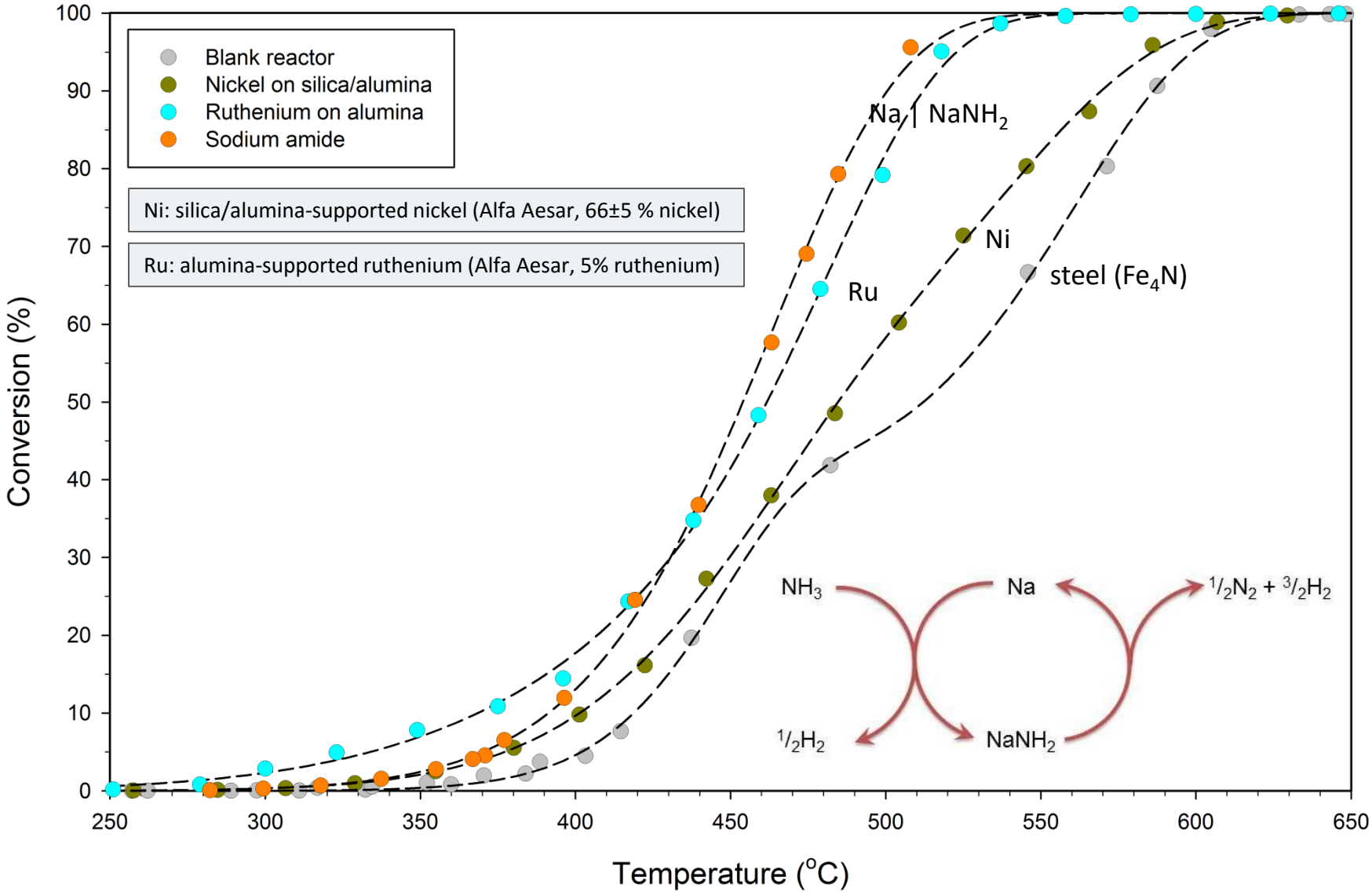
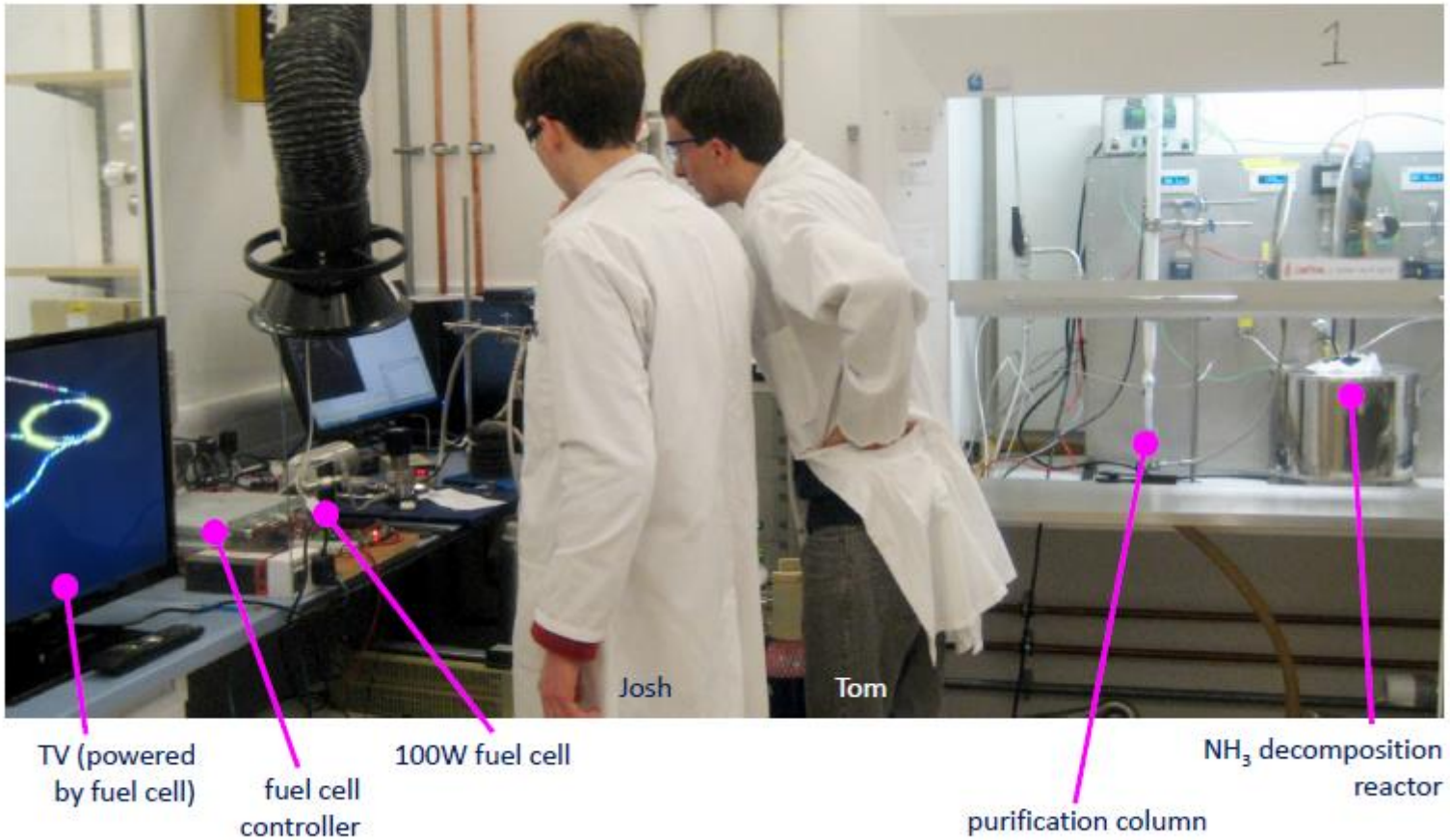
Ammonia cracking: $NaNH_2$ catalyst performance



WIF David, JW Makepeace *et al.* J. Am. Chem. Soc. **2014** 136(38) 13082-13085

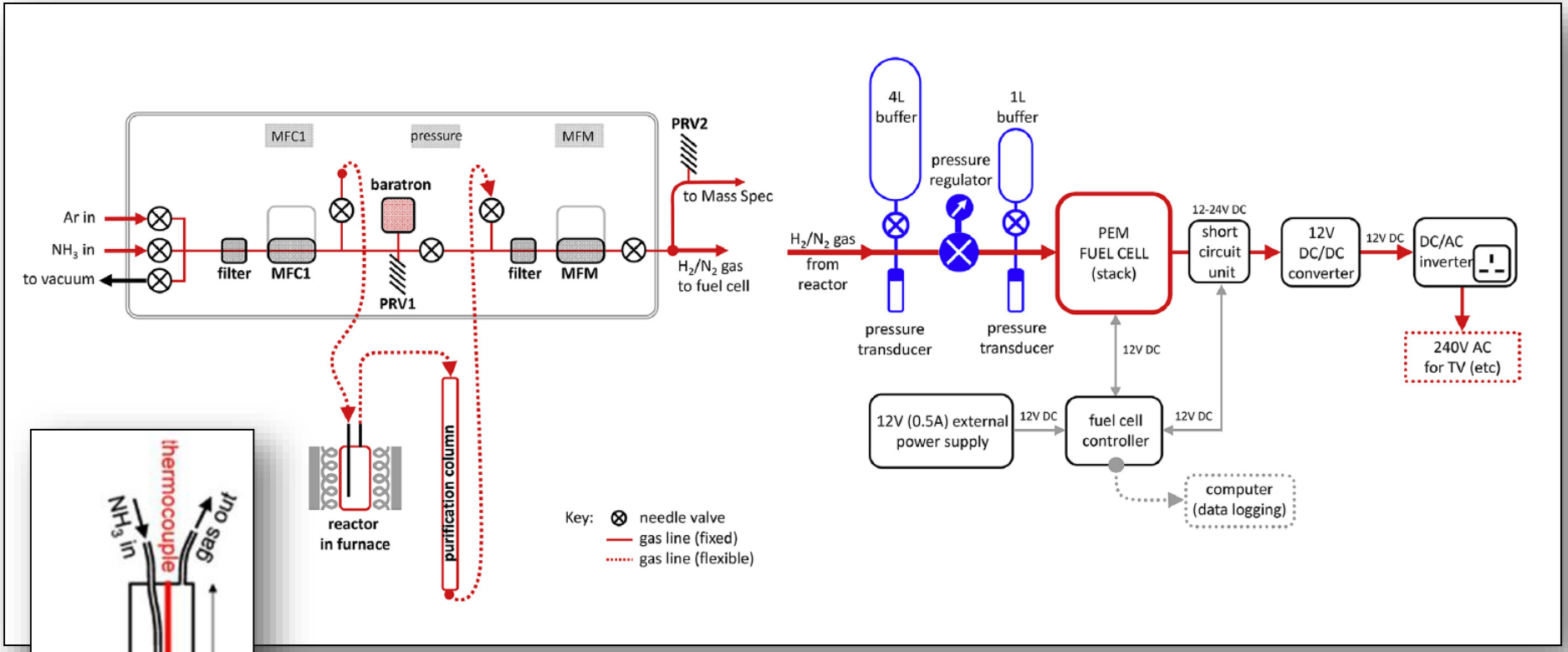
PEM fuel cell demonstrator

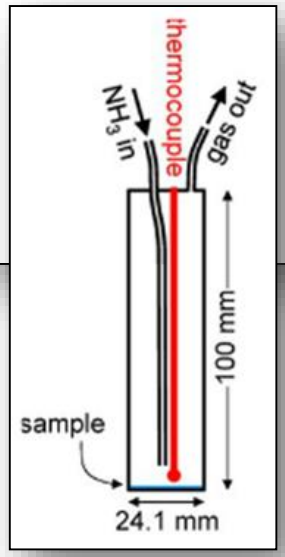


electricity ← 100W fuel cell ← purification ← reactor ← NH_3 gas in

HMA Hunter *et al.* Journal of Power Sources 329 (2016) 138-147 | dx.doi.org/10.1016/j.jpowsour.2016.08.004

PEM fuel cell demonstrator





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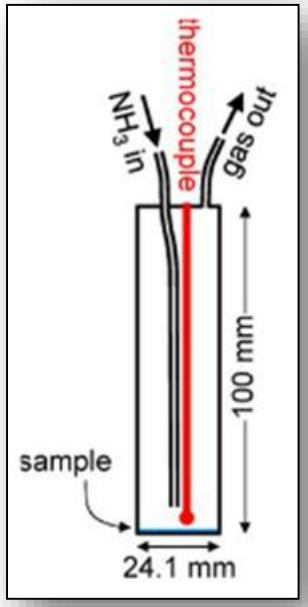
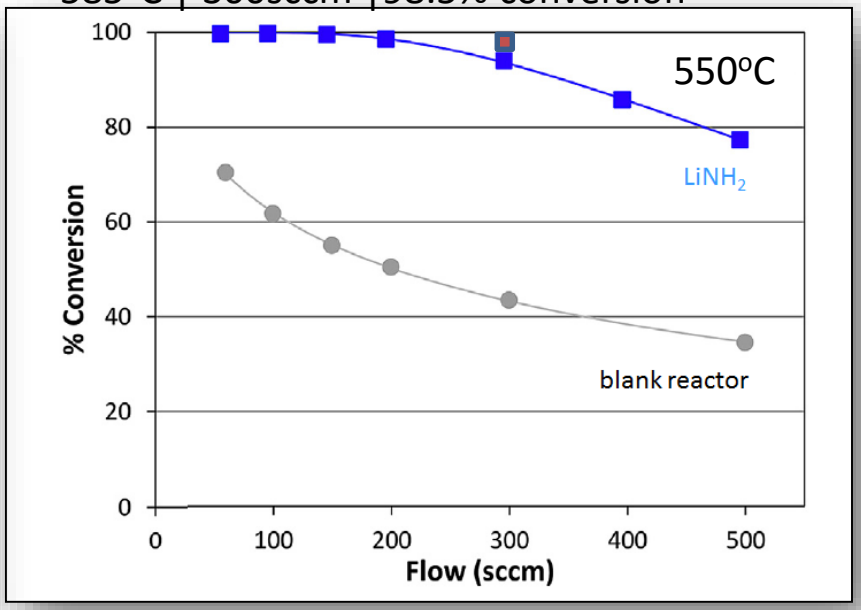
PEM fuel cell demonstrator: purification



585°C | 300sccm |98.5% conversion



$$MgCl_{2\,(s)} + 6NH_{3\,(g)} \rightarrow Mg(NH_3)_6Cl_{2\,(s)}$$

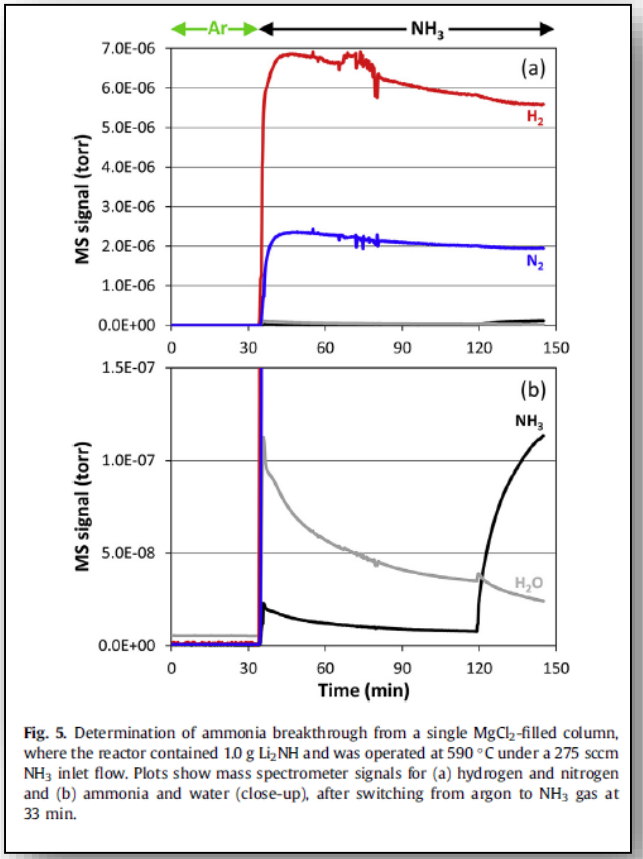
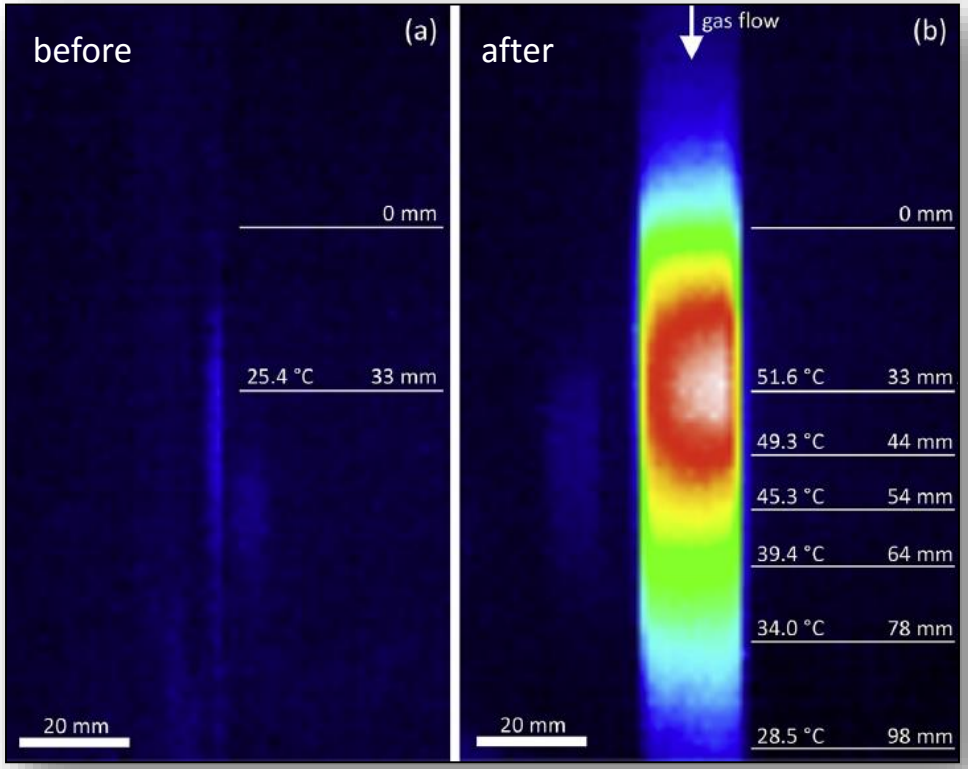


Fig. 5. Determination of ammonia breakthrough from a single $MgCl_2$-filled column, where the reactor contained 1.0 g Li_2NH and was operated at 590 °C under a 275 sccm NH_3 inlet flow. Plots show mass spectrometer signals for (a) hydrogen and nitrogen and (b) ammonia and water (close-up), after switching from argon to NH_3 gas at 33 min.

PEM fuel cell demonstrator: purification



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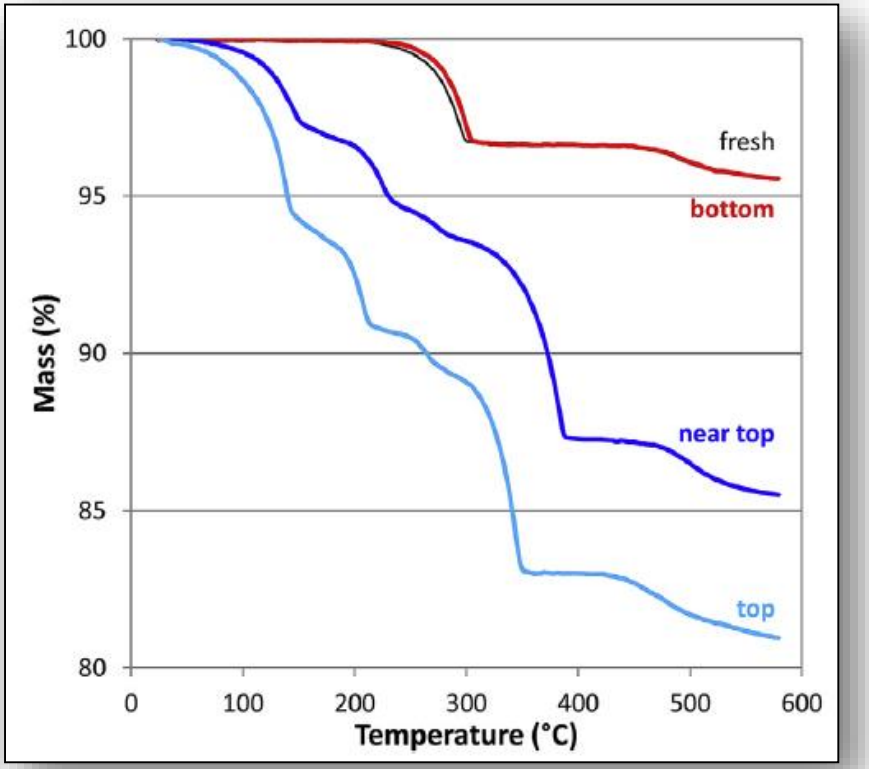
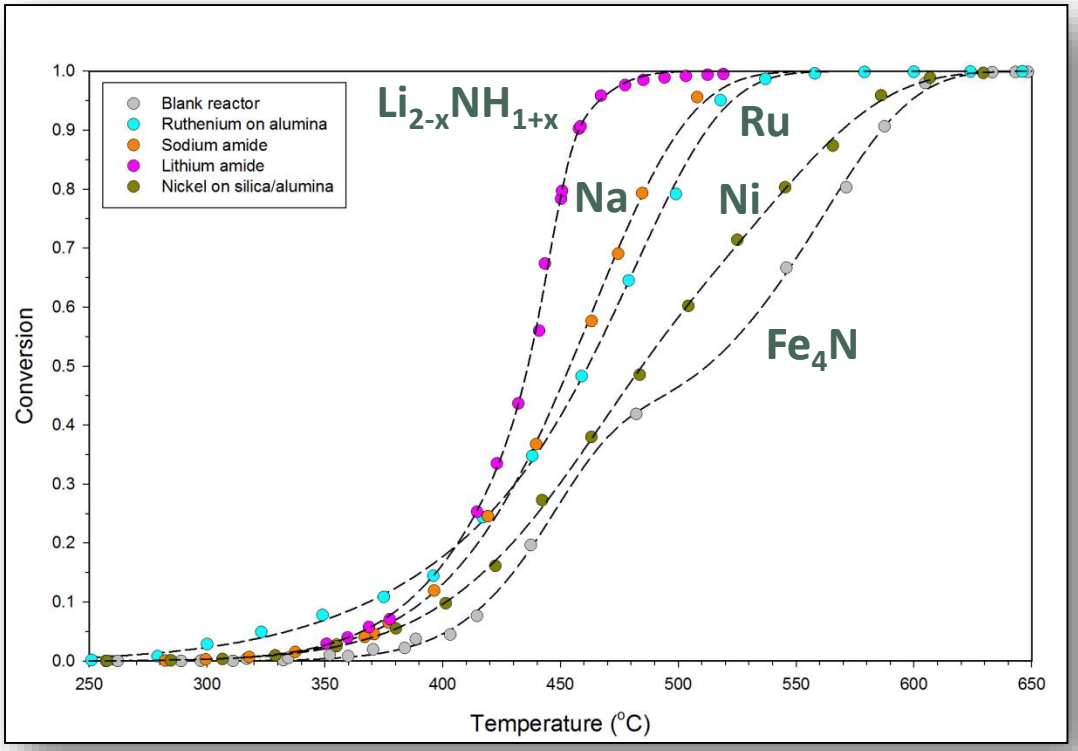


Ammonia cracking: $NaNH_2$ catalyst performance



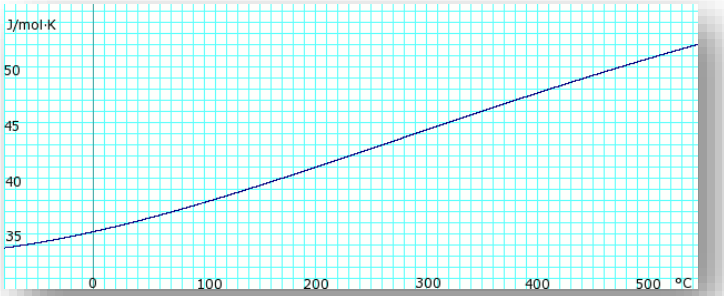
Next step:

1.0kW(nett)

1.5kW(gross) ≡ 10ℓ/m NH_3 (g)

≡ 0.4mol | 7.5gm | 12.5cm³ NH_3 (l)

NH_3 heat capacity



reactor volume | 21cm³

0.5g $Li_{2-x}NH_{1+x}$

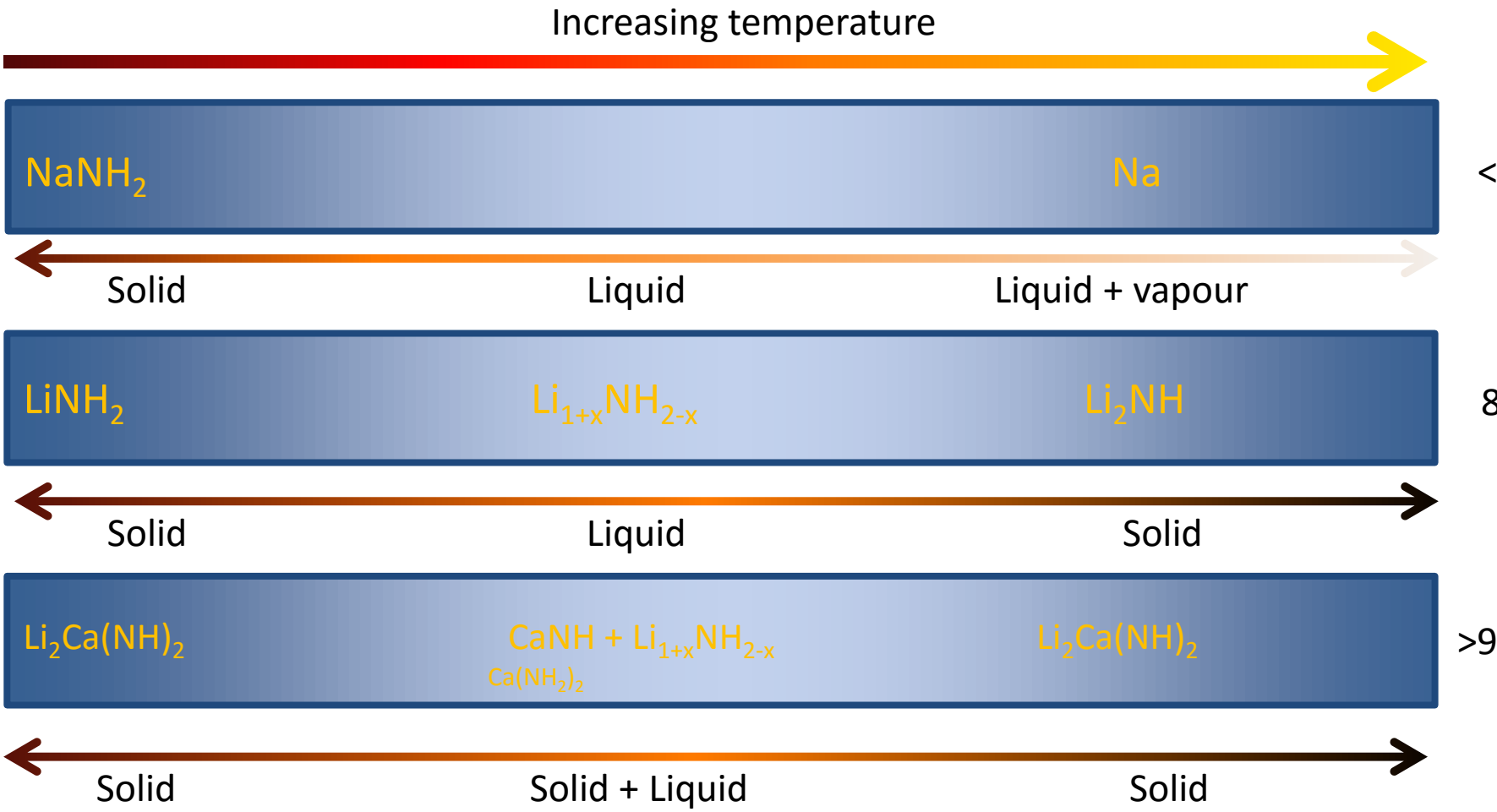
300sccm NH_3

450sccm H_2 | 45W

ΔT ≈ 500K | power required

P ≈ 500 × 42.5 × 0.4 / 60 ≈ 140W

Ammonia cracking: catalyst performance summary



Next steps: completely solid catalyst, improved decomposition kinetics, promotion…

STATUS & PROSPECTS

Catalyst development

- Solid catalyst
- Stable imide | unstable imide system

Catalytic reactor redesign

- Flow-through design
- Catalyst support

Purification

- materials improvement
- absorption reactor development

Fuel cell developments

- Anionic membrane alkaline fuel cells
- Purge strategies for $3H_2|N_2$ mixtures

Vision

- 5-10kW nett | remote telecommunications
- Partial conversion: additional combustion option
- Safe ammonia systems

ACKNOWLEDGEMENTS

Fuel Cell Demonstrator

Hazel Hunter	ISIS
Josh Makepeace	ISIS / Oxford
Tom Wood	ISIS
Kate Ronayne	STFC Innovations
Beth Evans	ISIS
Jamie Nutter	ISIS
Mark Kibble	ISIS
Richie Haynes	ISIS
James Taylor	ISIS

Catalysts

Josh Makepeace	ISIS / Oxford
Martin Jones	ISIS
Hazel Hunter	ISIS
Tom Wood	ISIS

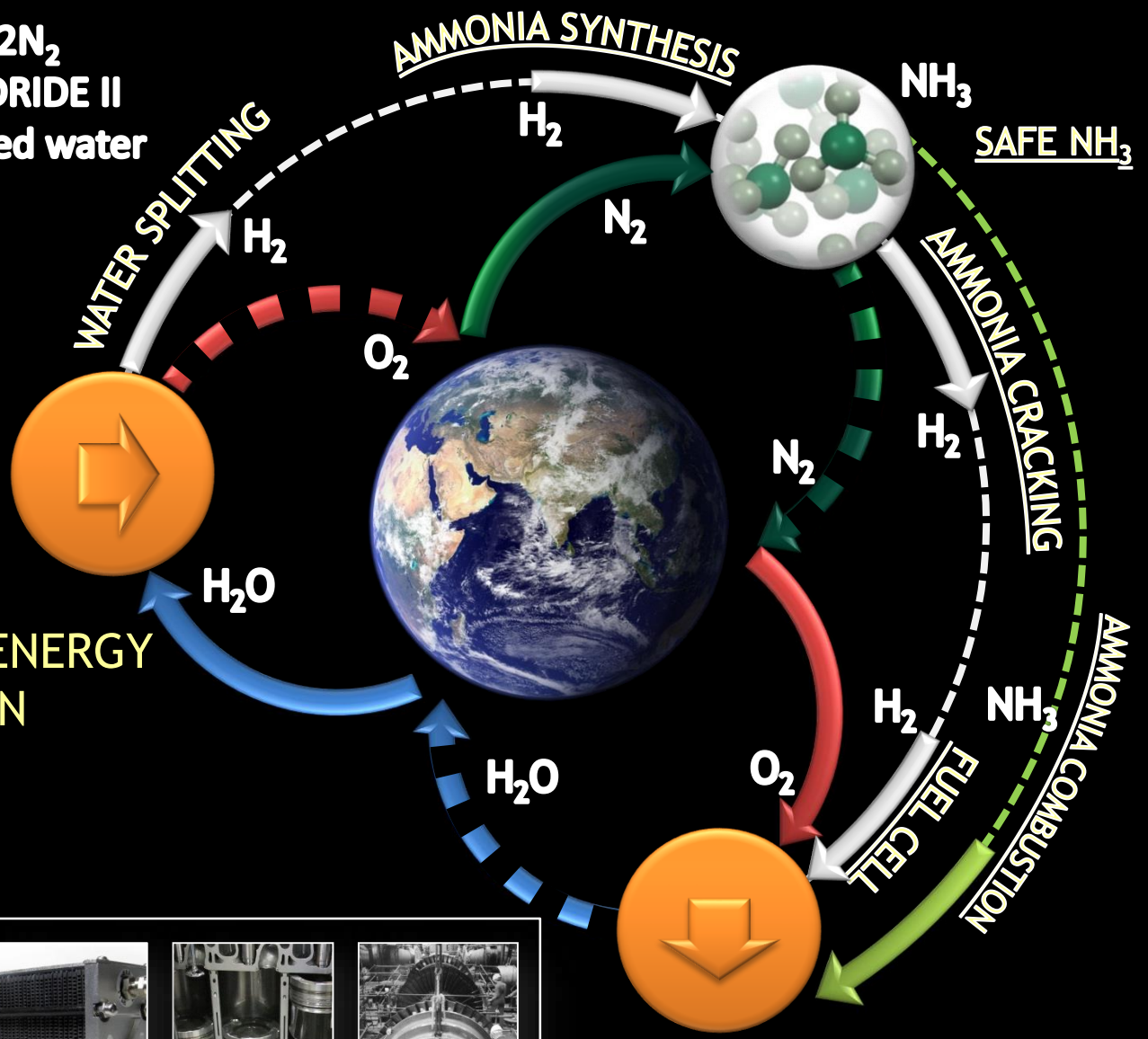
Ammonia + Anionic membrane AFCs

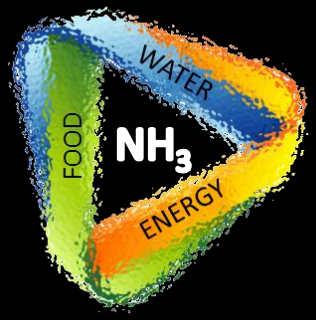
Tom Wood	ISIS
Josh Makepeace	ISIS / Oxford
Martin Jones	ISIS
Dan Brett	UCL
Paul Shearing	UCL
John Varcoe	Surrey

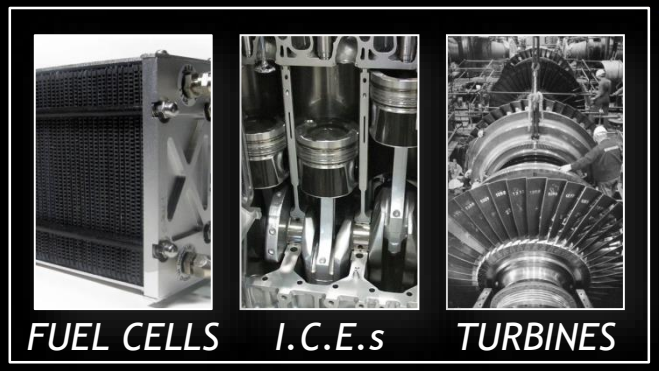
$4NH_3 + 3O_2 \leftrightarrow 6H_20 + 2N_2$

AIR HYDRIDE I ↔ AIR HYDRIDE II

water ↔ energised water







THE WATER : AMMONIA CYCLE