Solid ammonia storage technology for fuel cell systems

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Amminex A/S, Denmark

Ammonia: a sustainable emisson-free fuel, 2007

AMMINEX
Ammonia Enabling Technologies

Energy storage for fuel cell applications

- Energy source ?
  - Sustainable use of fossil fuels (incl. coal)?
    - Central production of C-free energy carrier with CO_2 seq.
  - Renewable paths to energy production and storage

- Examples of carbon-free energy carriers
  - Hydrogen
  - Electricity (incl. batteries)
  - Ammonia

- Energy conversion
  - ICE
  - Electric motor
  - Hydrogen fuel cell (PEM)
  - SOFC
  - Other fuel cells

Hydrogen storage

- Liquefied H_2
  - Boil-off, cost of liquefying, safety
- High pressure H_2
  - 500 bars needed, cost of compression, safety
- Metal hydrides, e.g. MgH_2
  - Limited bulk density, kinetics
- Complex hydrides, e.g. $NaAlH_4$, Li…
  - kinetics/catalyst, synthesis, reversibilit…
- Chemical hydrides
  - Expensive materials, rever… system
- Physisorption in … …ials
  - Material dev… …esis routes, gravimetric and volumetric density

Advantage: delivery of pure H_2

Fuel comparisons

Fuel	Base MJ/liter	Reformed MJ/liter*
H_2 (5000 psia)	4.0	4.0
H_2 (liq.)	9.9	9.9
NH_3 (liq.)	15.3	13.6
Methanol	17.9	10.2
Ethanol	23.4	9.1
Propane (liq.)	29.4	8.6
Gasoline	36.2	9.2
JP-8	40.5	9.7

* Includes heat and water volume required for steam reforming
J. Ganley, Ammonia Fuel III, 2007

So why not ammonia?

- Dense liquid; ~ 18% of hydrogen
- Optimized catalyst exist
- Easy to reform to H_2: single reactor

- But liq. NH_3 is normally considered too dangerous: > 6 bar of vapor P. at RT

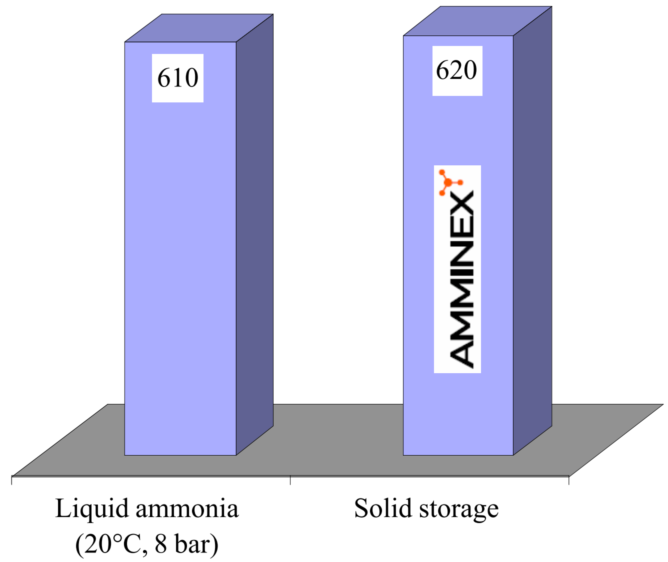
Core technology – metal ammine complexes

- Safe storage of ammonia in proprietary storage cartridges
- Controlled release with low energy consumption
- Volumetric capacity comparable with liquid ammonia

• 100g "block"; 51.7g NH_3 stored
• 74 liter NH_3(g) @ 20°C; 1 bar
• The equivalent ammonia gas pressure would be almost 900 bar

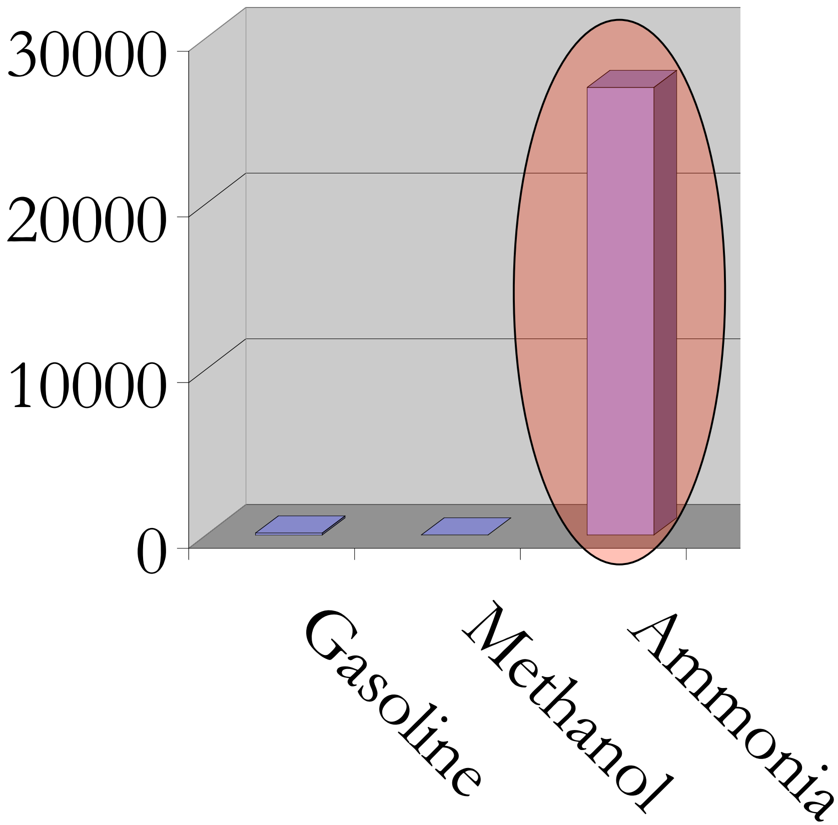
e.g. $Mg(NH_3)_6Cl_2$ or $Ca(NH_3)_8Cl_2$

Ammonia capacity (measured in kg/m^3)

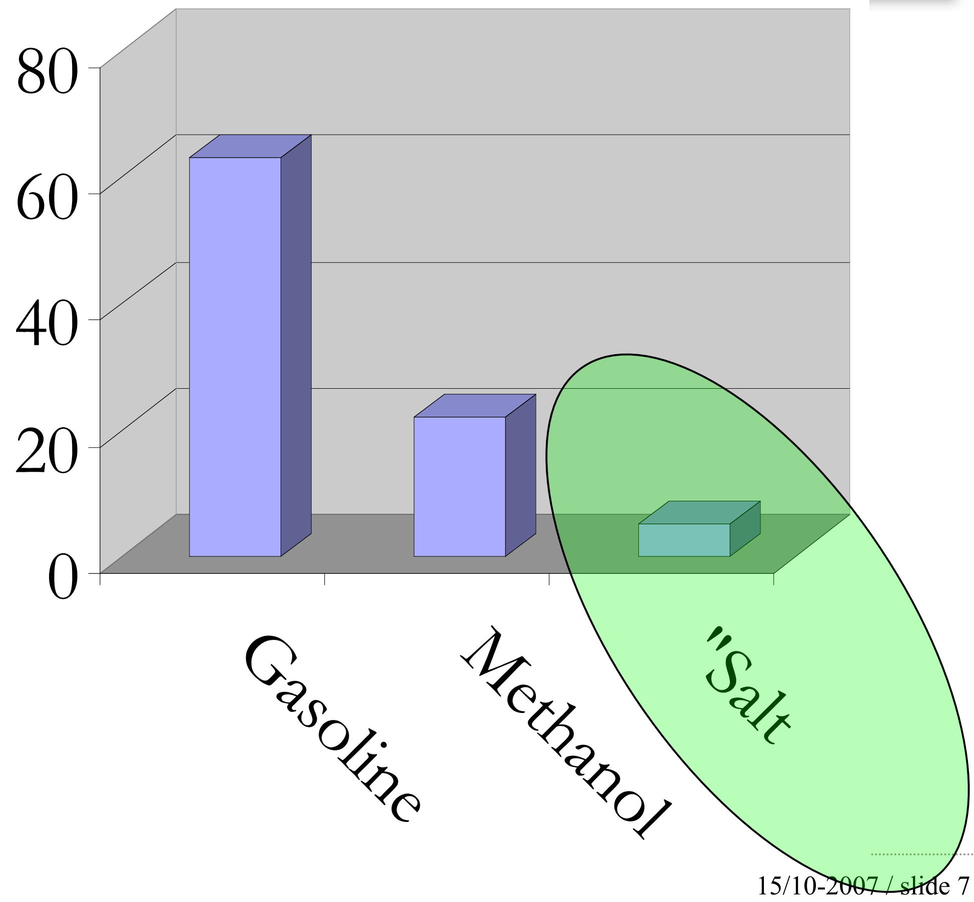


• Ammonia vapor pressure at room temperature: **as low as 0.004bar**;
• Comparable to 0.5% aqueous ammonia ("Ajax")

Volatility-to-toxicity ratio*

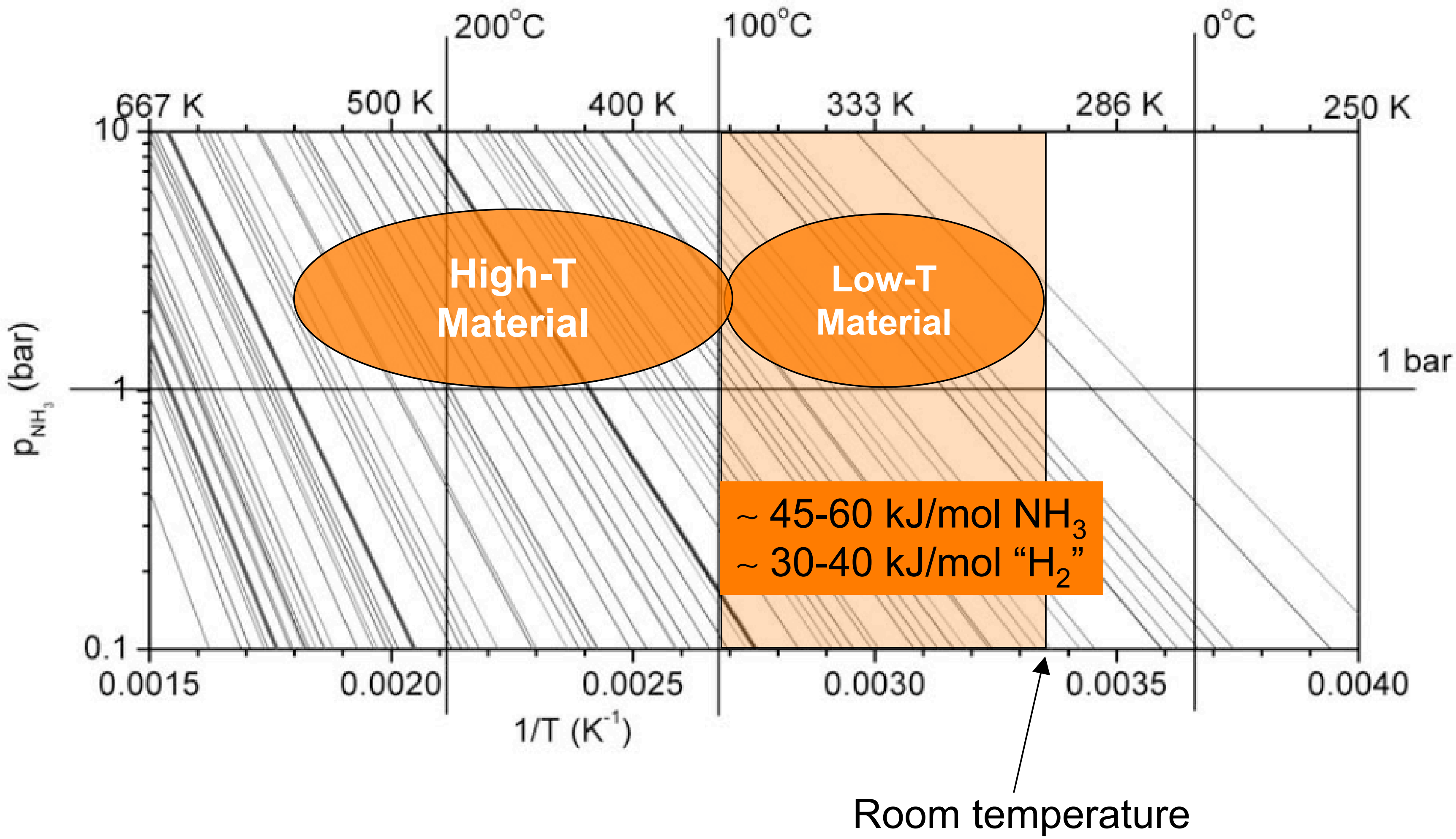


1 liter liquid ammonia
=> 1.1 liter storage material
=> 1.3 kg storage material
=> 4000 times lower volatility



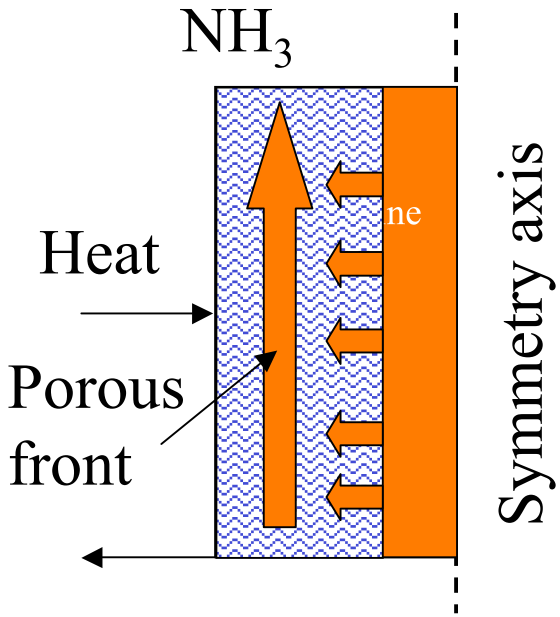
* Vapor pressure divided by IDLH (NIOSH) partial pressure

A wide range of storage materials



Releasing NH_3 from dense storage units

Ammonia release by controlled thermal desorption



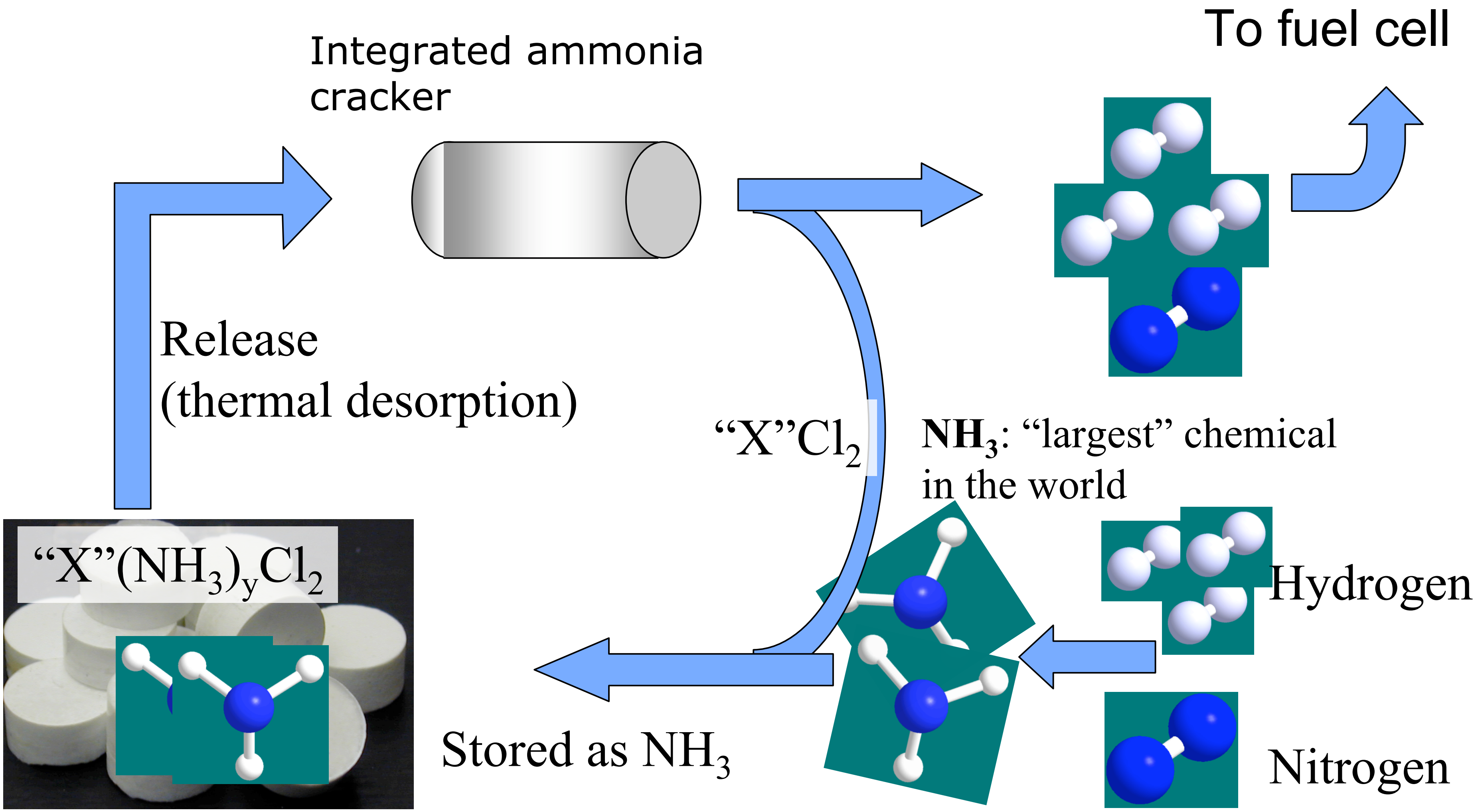
Core technology applications

Ammonia-based hydrogen generation for fuel cell systems

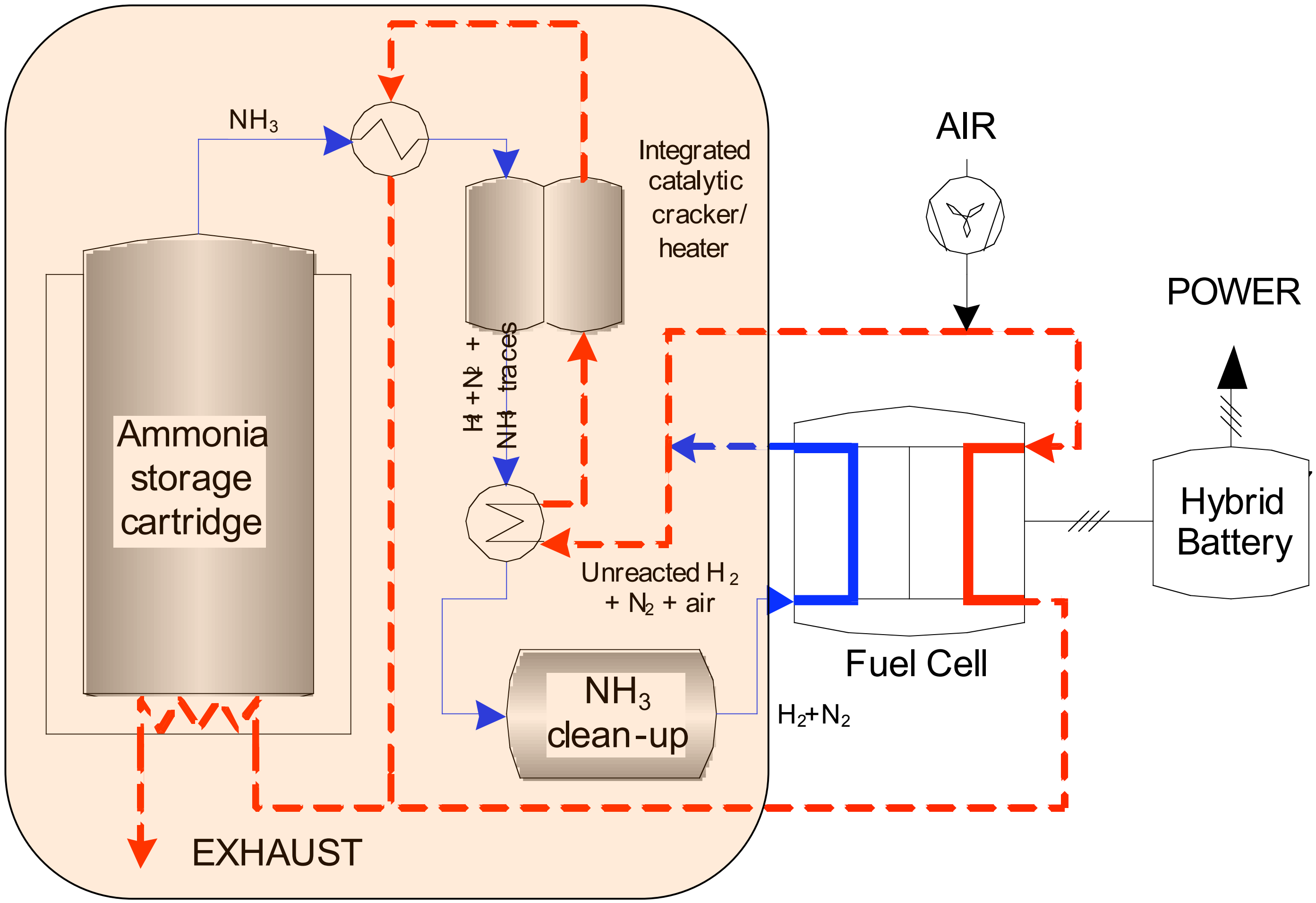
Ammonia storage and delivery systems for automotive SCR-DeNOx

Energy storage applications

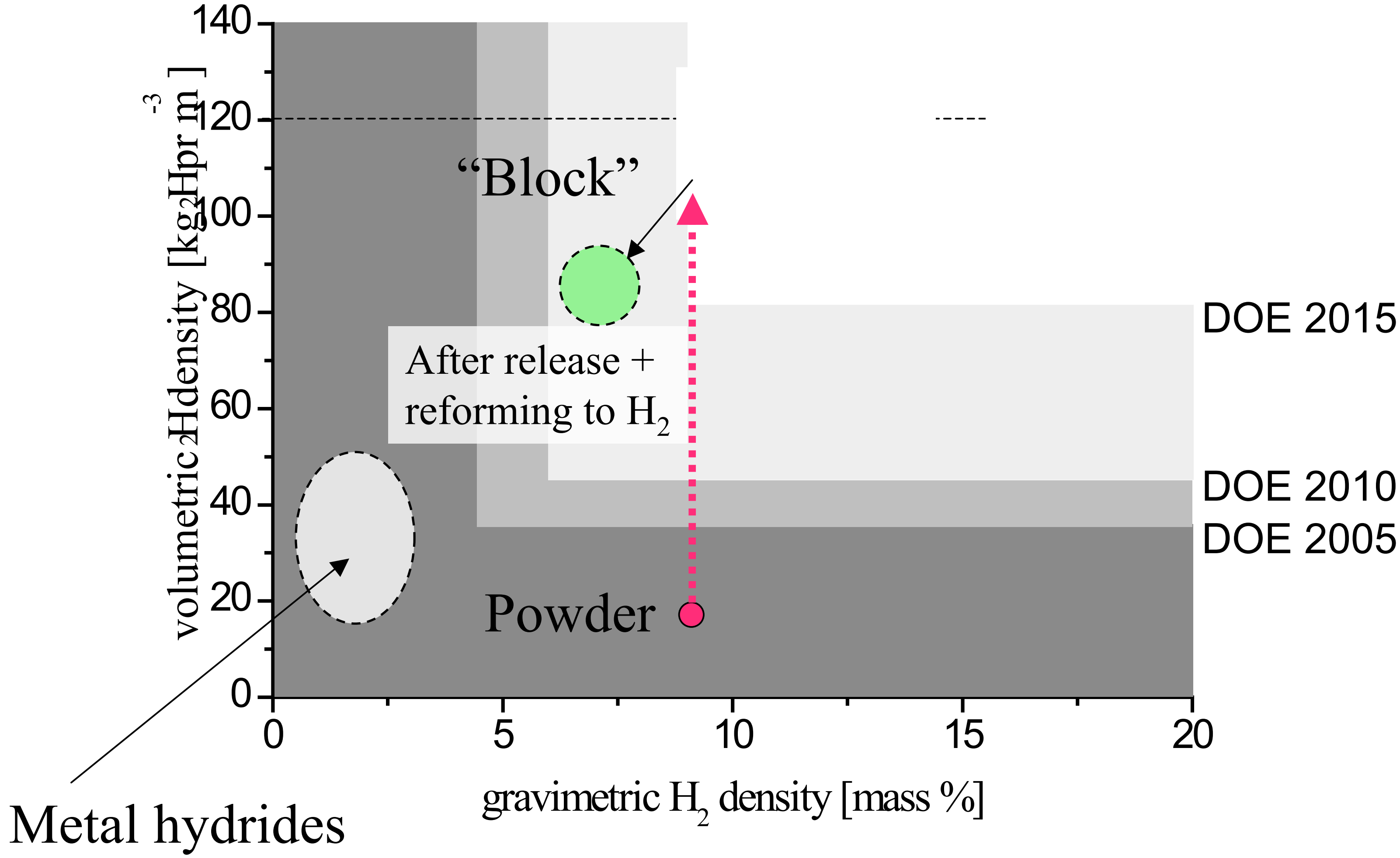
Focusing on hydrogen



Amminex technology with PEM-FC



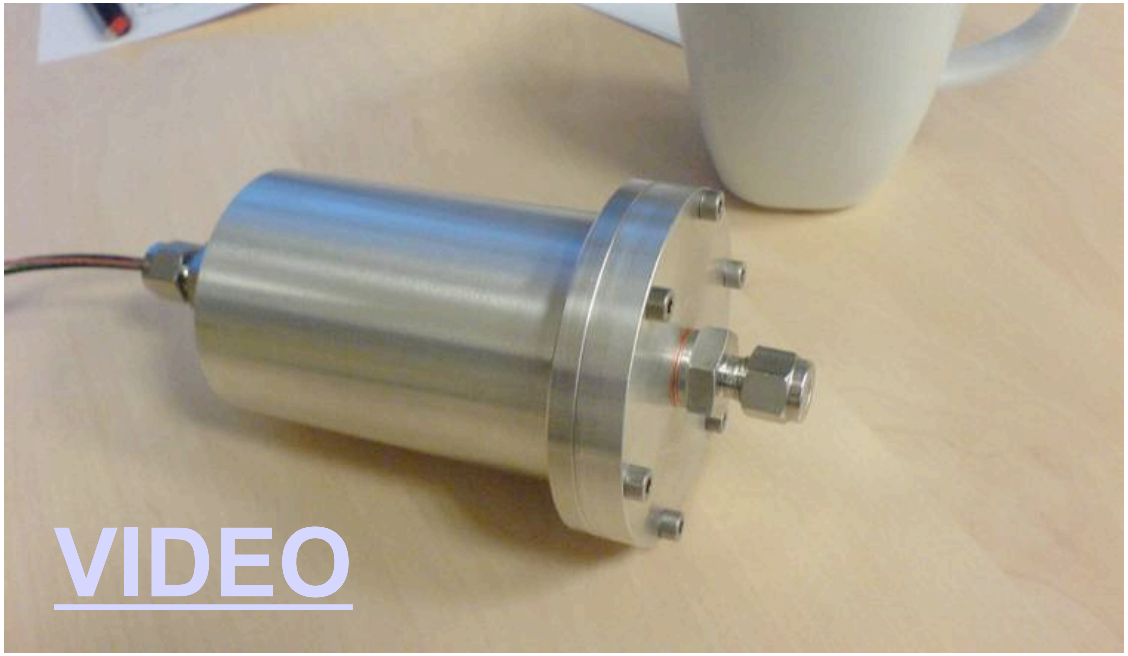
Corresponding hydrogen storage capacity



*data based on material, not system

Plug 'n' play ammonia delivery unit

- Capacity of demo unit: 100g NH_3
- For demo-purposes: operated by electricity (plug directly into the "wall")
- 40-45W; 1.2 nL NH_3 (gas) per minute
- Safe and simple ammonia delivery
- Low operating temperature (compatible with PEMs)
- Low pressure (safe)



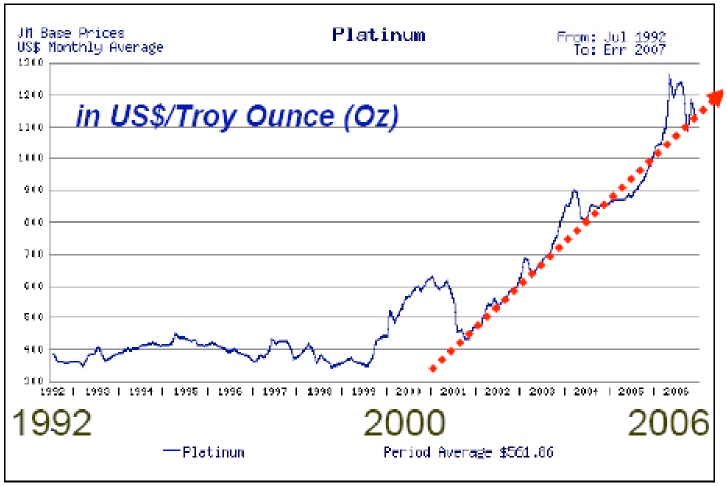
Integration with PEMs: Combining demonstrated technologies

- Ammonia storage
- Catalytic ammonia cracking
- Removing NH_3 traces (for PEM)
- Fuel cell stack
- Heat management & BoP

BUT: Hydrogen storage is mainly suited for PEM;
Cost of PEMs is tied up with Pt-prices

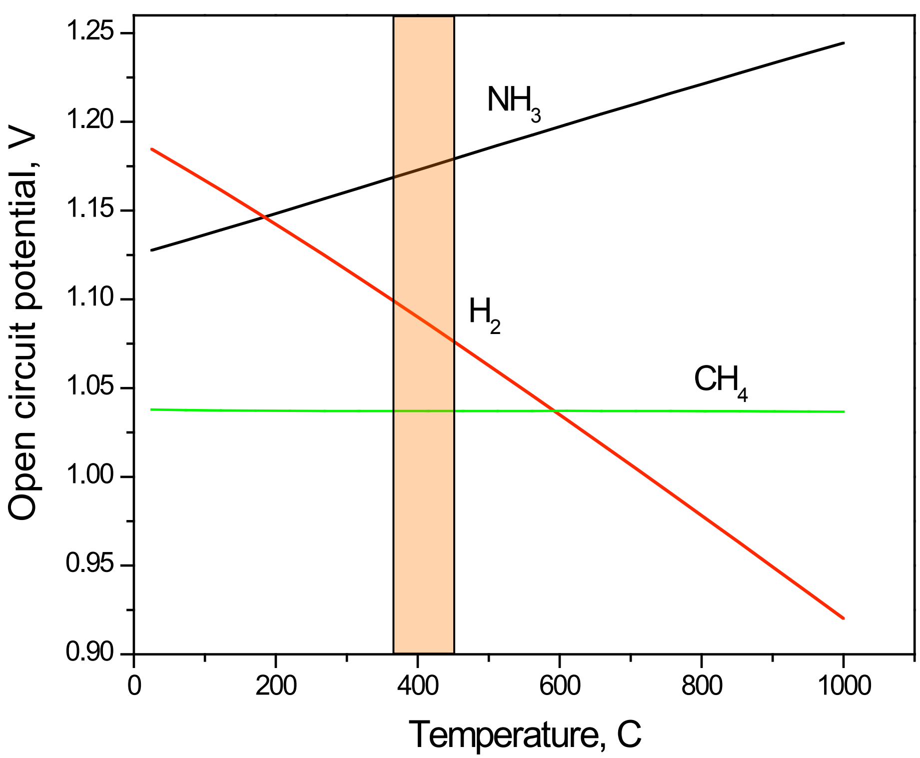
(in US$/Oz)	**Pt**	**Rh**
1992	**360**	**2700**
2006	**1200**	**5500**

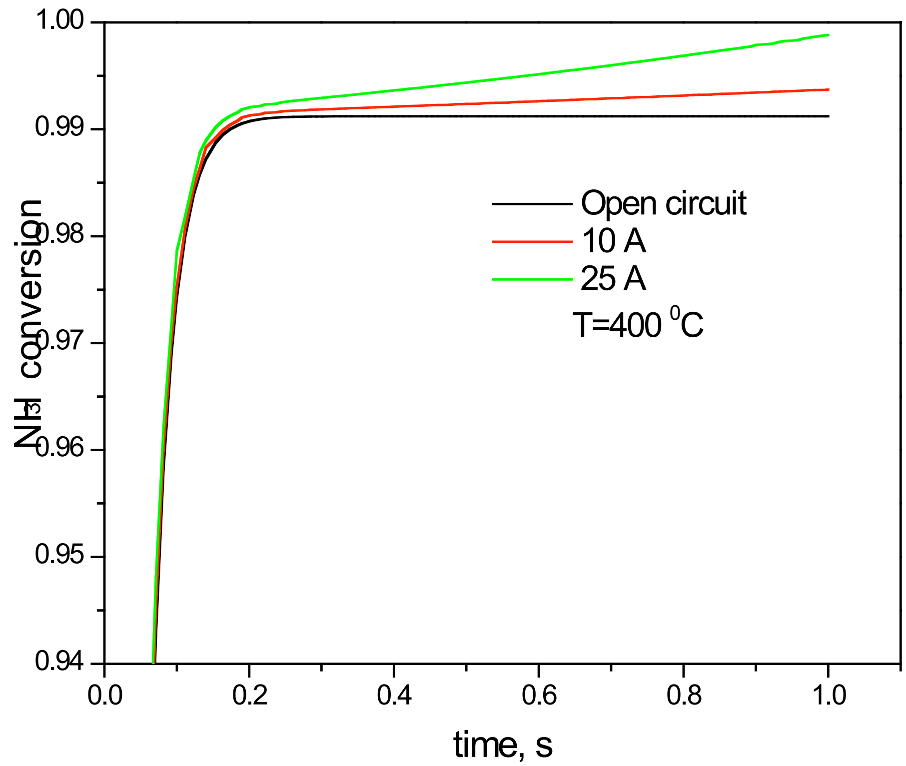
Source: www.platinum.matthey.com/ Jan.22, 2007



Other types of fuel cells

Ammonia as FC feedstock





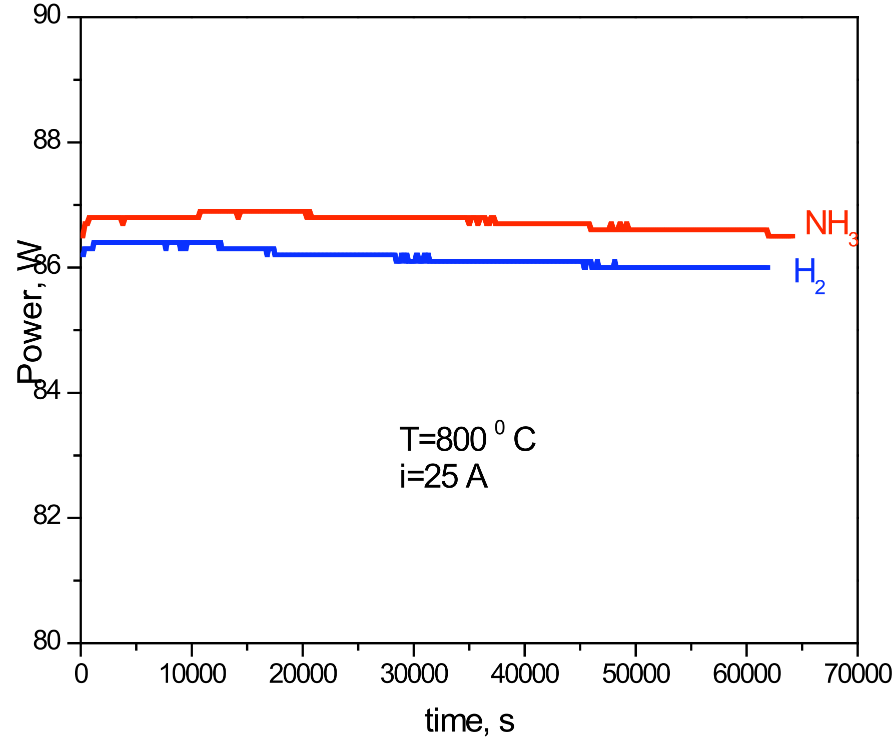
H_2 and CH_4 from:
High Temperature Solid Oxide Fuel Cells – Fundamentals, Design and Aplications, S.C. Singhal & K. Kendall (2003) Elsevie

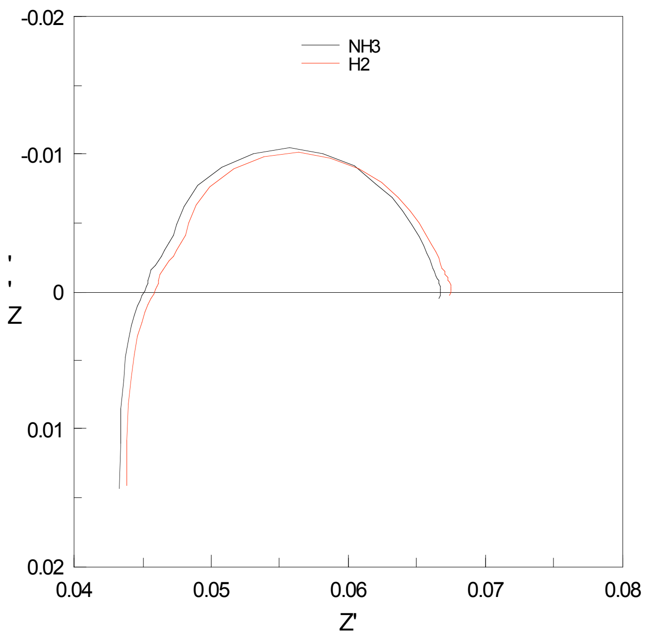
Highest OCP above 200 C

E.g at 400 C, almost total conversion of NH_3 can be achieved in an ammonia fuel cell.

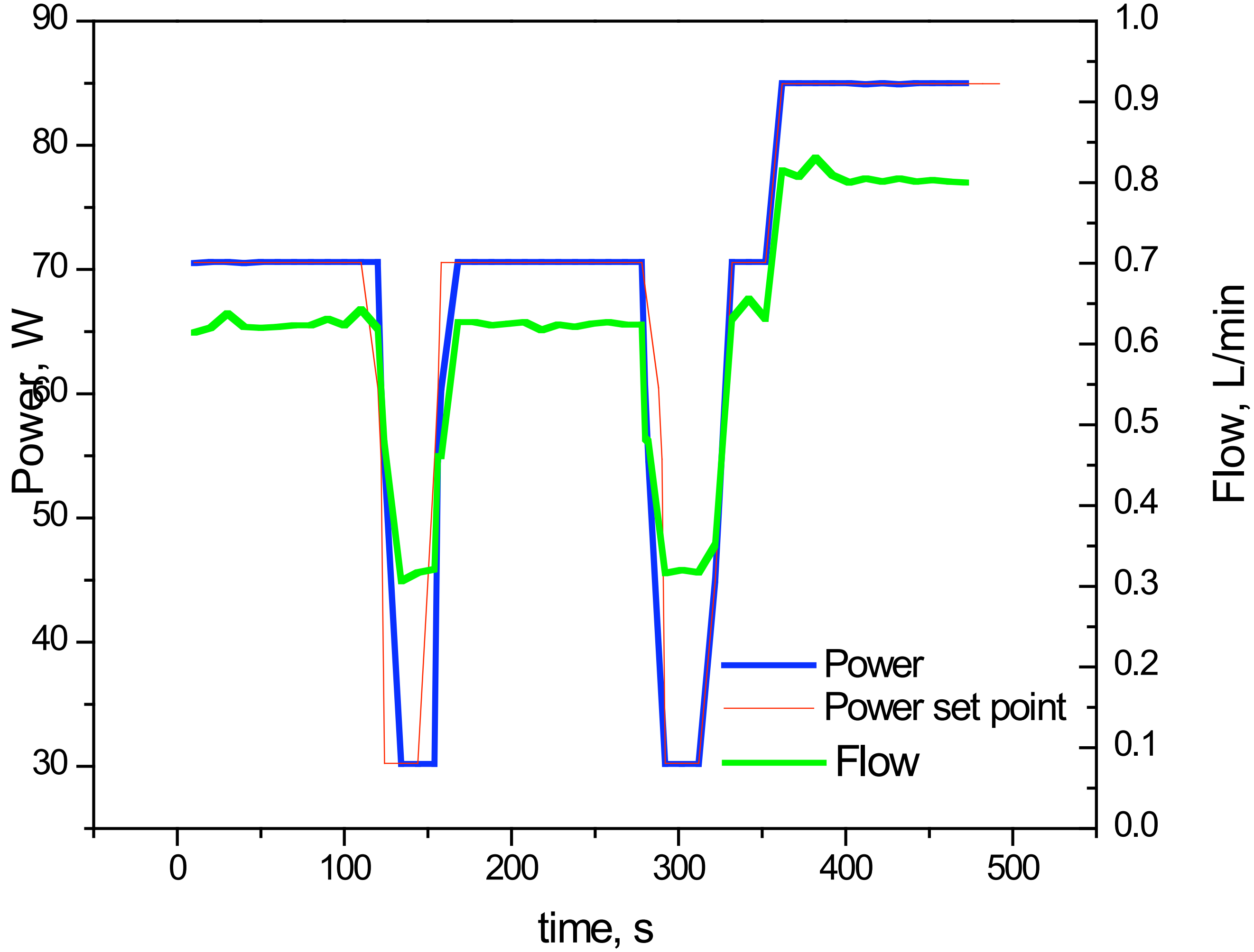
Ammonia as SOFC feedstock

- ❑ 5 cells stack from TOPSØE FC
- ❑10 cm x 10 cm cell





Dynamic load



FC system overview

HydrAmmine $\rightarrow NH_3 \rightarrow H_2 + N_2 \rightarrow$ High-T PEM FC

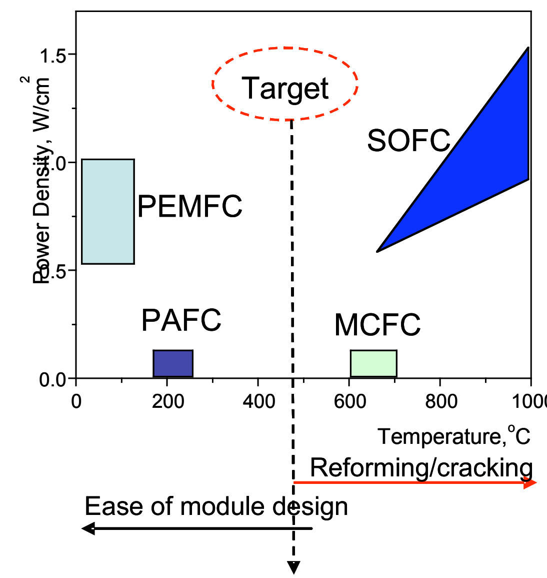
Waste heat / burner

HydrAmmine $\rightarrow NH_3 \rightarrow$ DAFC

Waste heat

HydrAmmine $\rightarrow NH_3 \rightarrow$ SOFC

Waste heat



*"New leads for future vehicles: **Intermediate temperature fuel cell** and new hydrogen storage materials"*, S. Iguchi, N.Ito, K. Kimura, K. Tange, H.Suzuki, **Toyota Motor Corporation**, Fuel Cell Seminar2004, San Antonio, Texas.

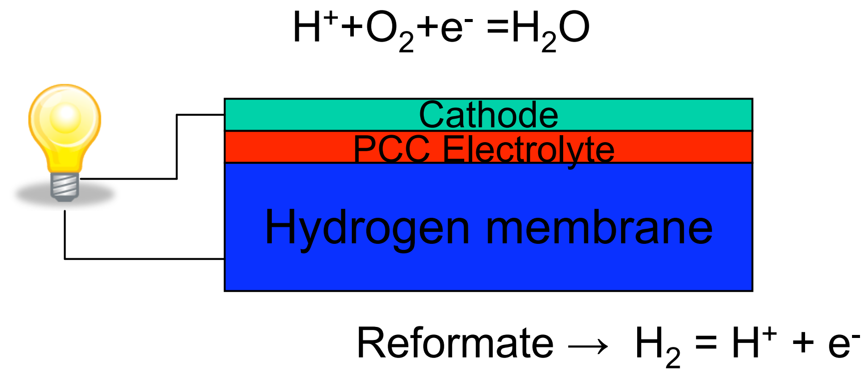
Basis for intermediate-T fuel cells: PCC

Developments by Toyota

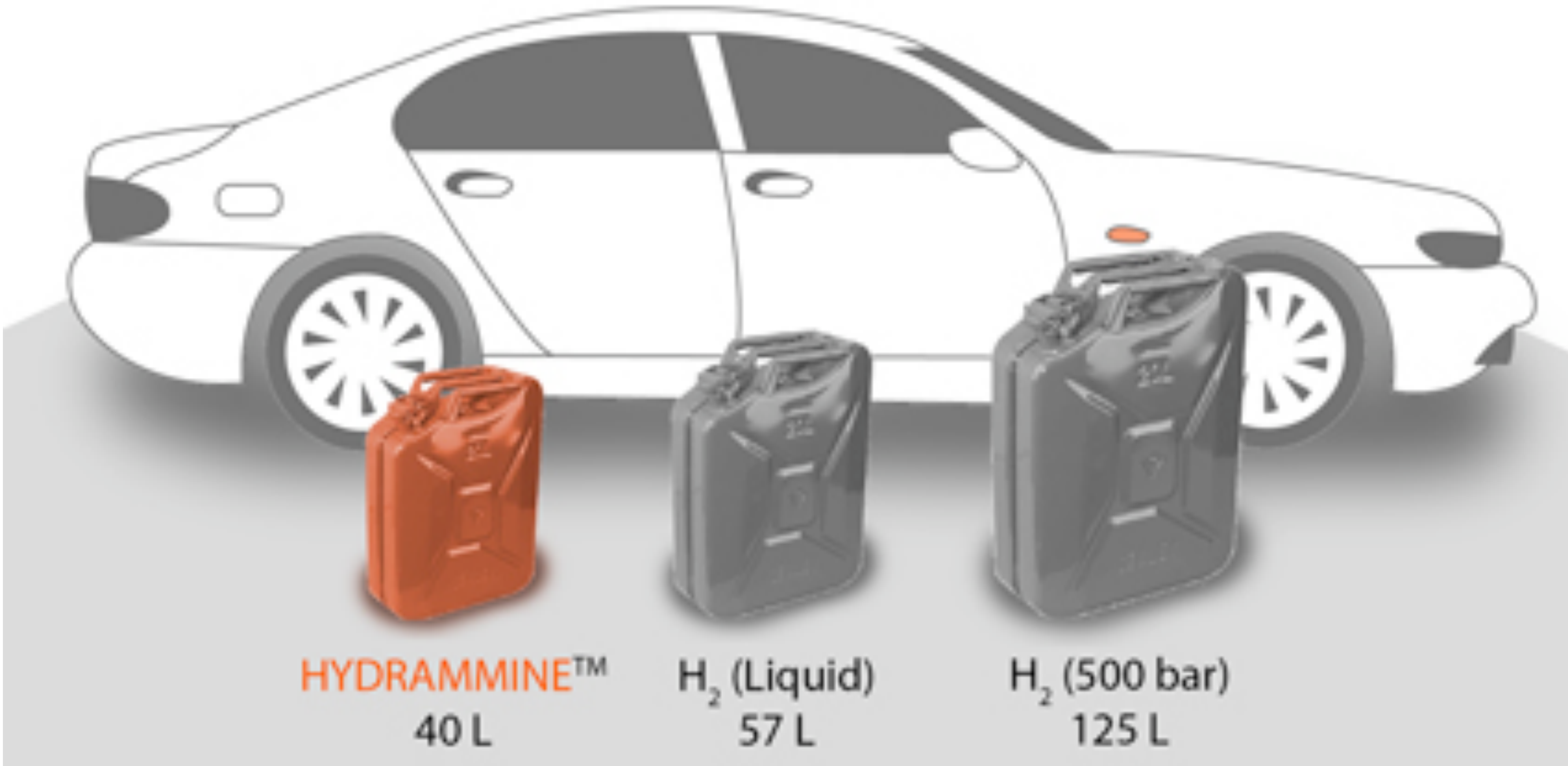
PCC electrolyte.

Reformate feedstock ⇒ Needs a thick

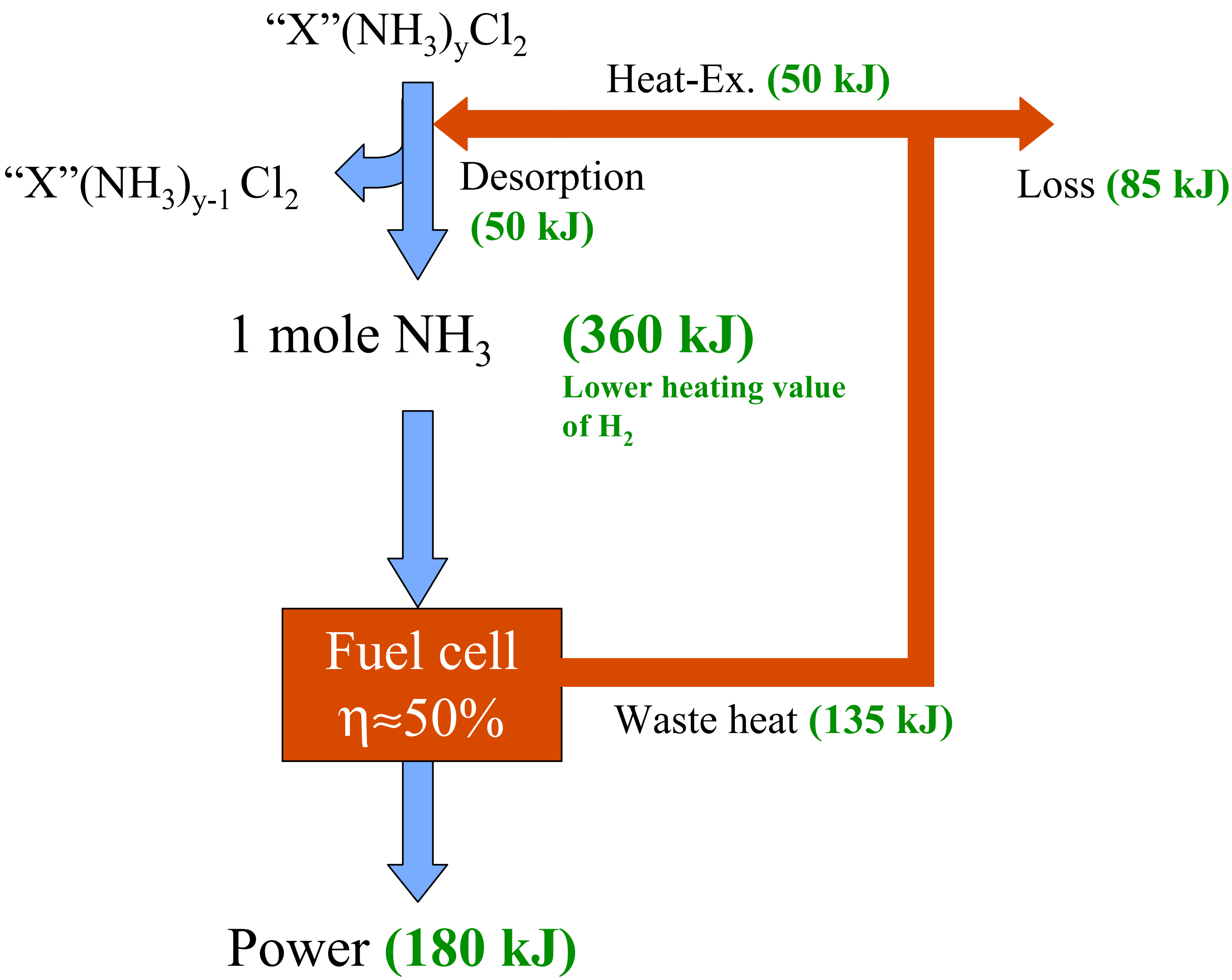
Pd membrane ⇒ performance ↓ and cost ↑



Energy density comparison

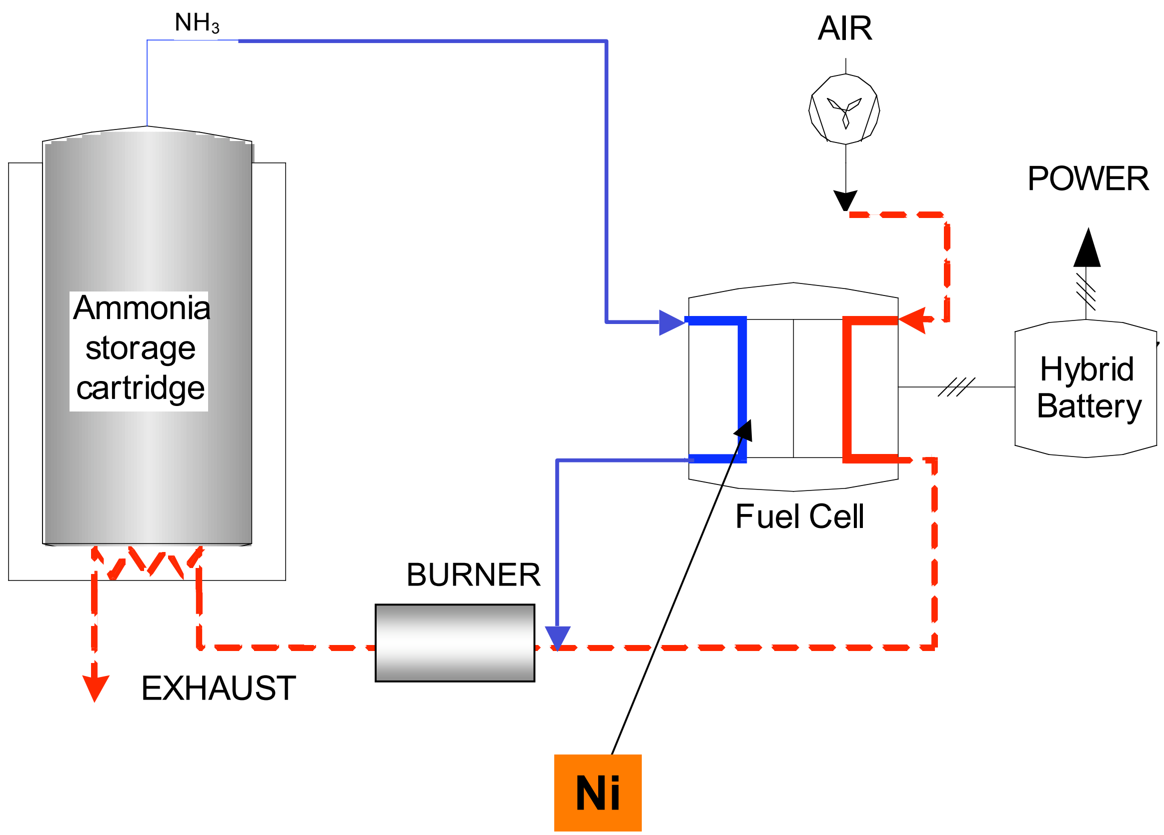


Heat integration – DAFC



HydrAmmine + DAFC : simplifying the system layout

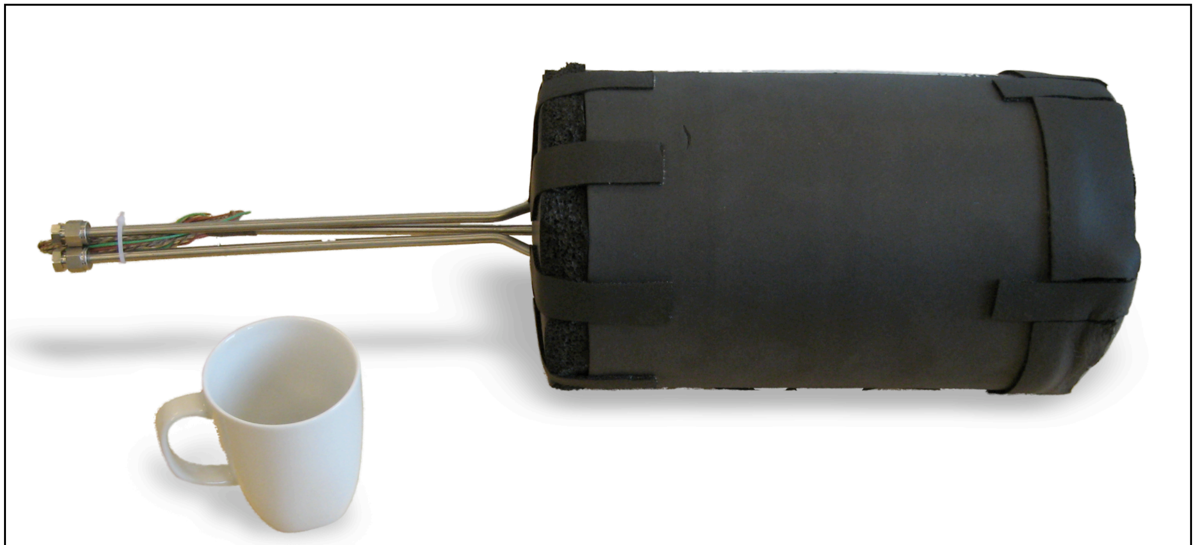
HydrAmmine + DAFC
HydrAmmine + PEMFC



NH_3 storage cartridge: 4kg prototype has been developed

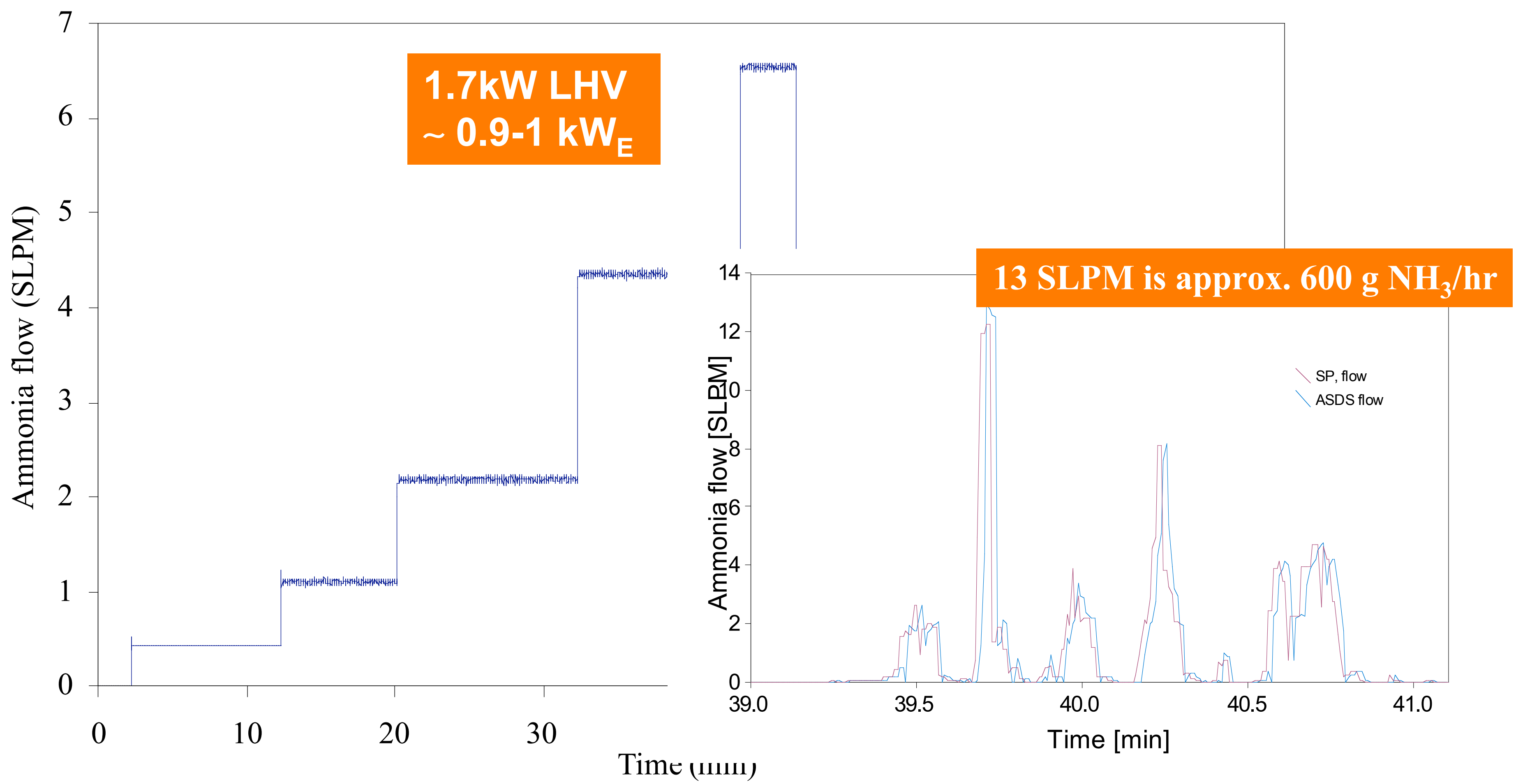
Prototype 4 kg Low-T HydrAmmine storage cartridge. Capacity is close to 2kg NH_3 *(approx. 2500 liters* NH_3 *gas can be released).*

Coffee mug for scale.

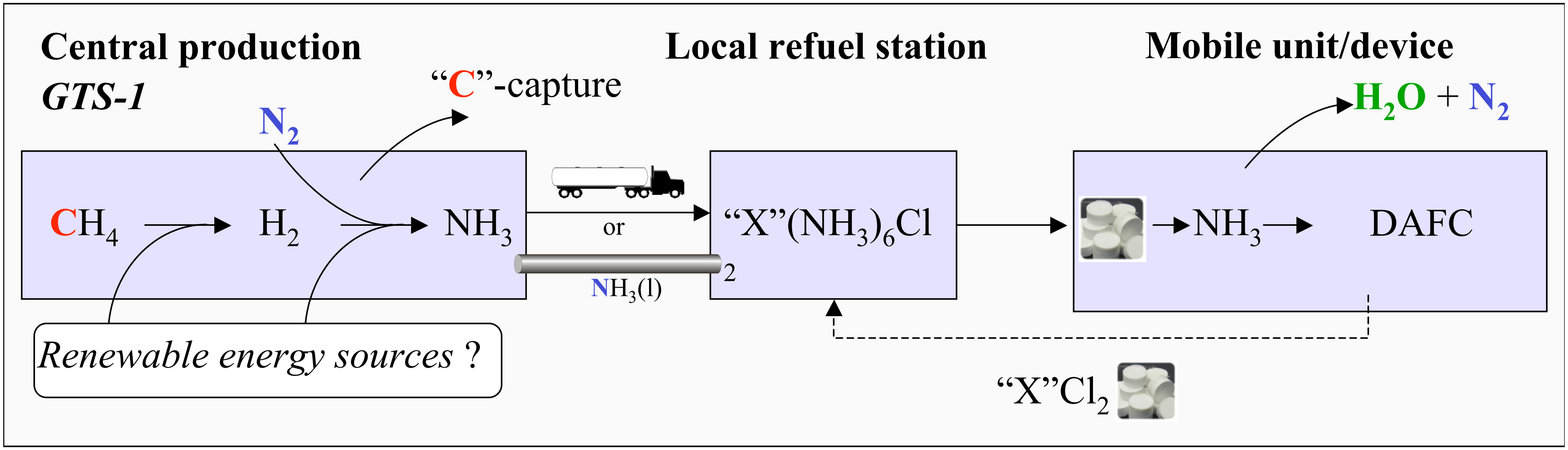


Dynamic ammonia release for fuel cell applications

- Dynamic dosing as well as high continuous flow rates.



Infrastructure



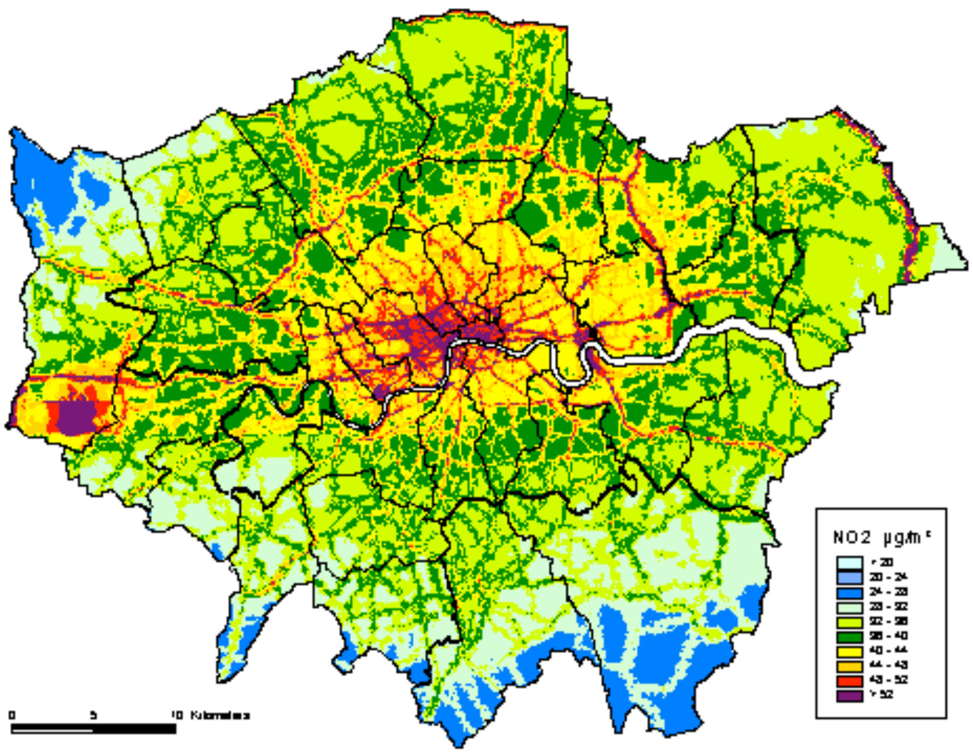
Possibilities for automotive fuel cell systems

- Suitable fuel cell operating temperature
- No platinum required for anode
- Carbon-free energy storage
- Low-cost, high-density storage concept
- Mature infrastructure for ammonia
- Safe, low-pressure storage
- Efficient integration with fuel cell system

While we are waiting for the fuel cell era...

The NOx / CO_2 paradox

Diesel/lean-burn engine: → 20-40 % improved fuel economy
→ less CO_2-release per km.
→ more particles and NOx emission



NOx-map of London

Solution:

Exhaust gas clean-up by SCR

Selective catalytic reduction

Selective catalytic reduction of NO_X

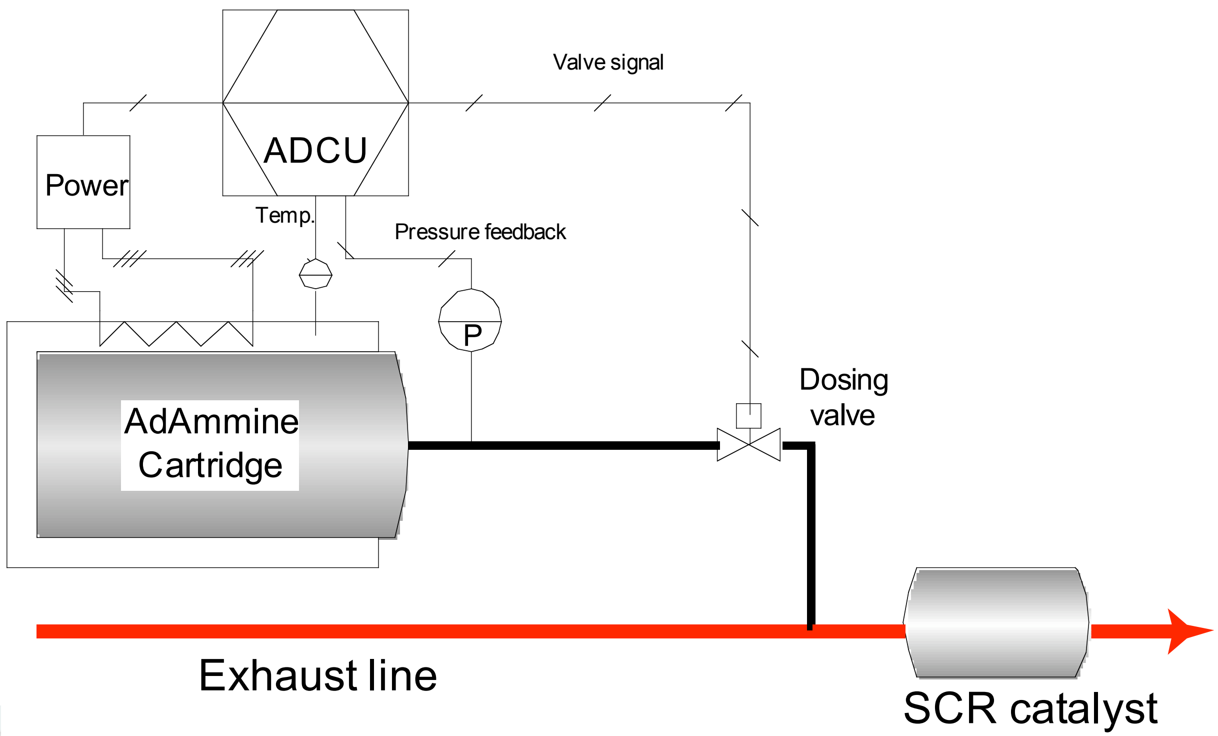
a) **$4NH_3$** $+ 4NO + O_2 \rightarrow 4N_2 + 6H_2O$

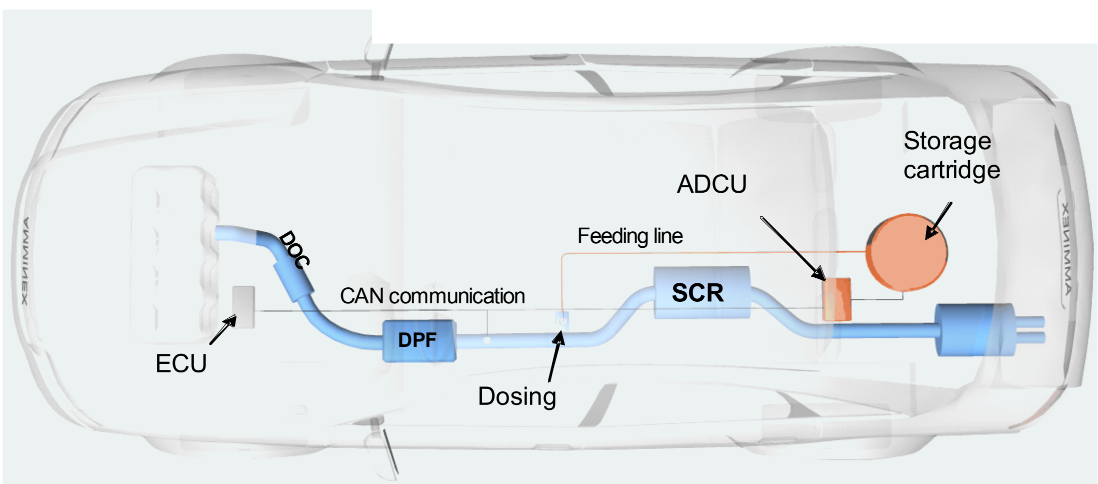
b) **$4NH_3$** $+ 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$

Optimal reductant: **Direct ammonia dosing**

But: Pressure vessel (8-9 bar at RT) with liquid ammonia is not an acceptable method for on-board NH_3 storage.

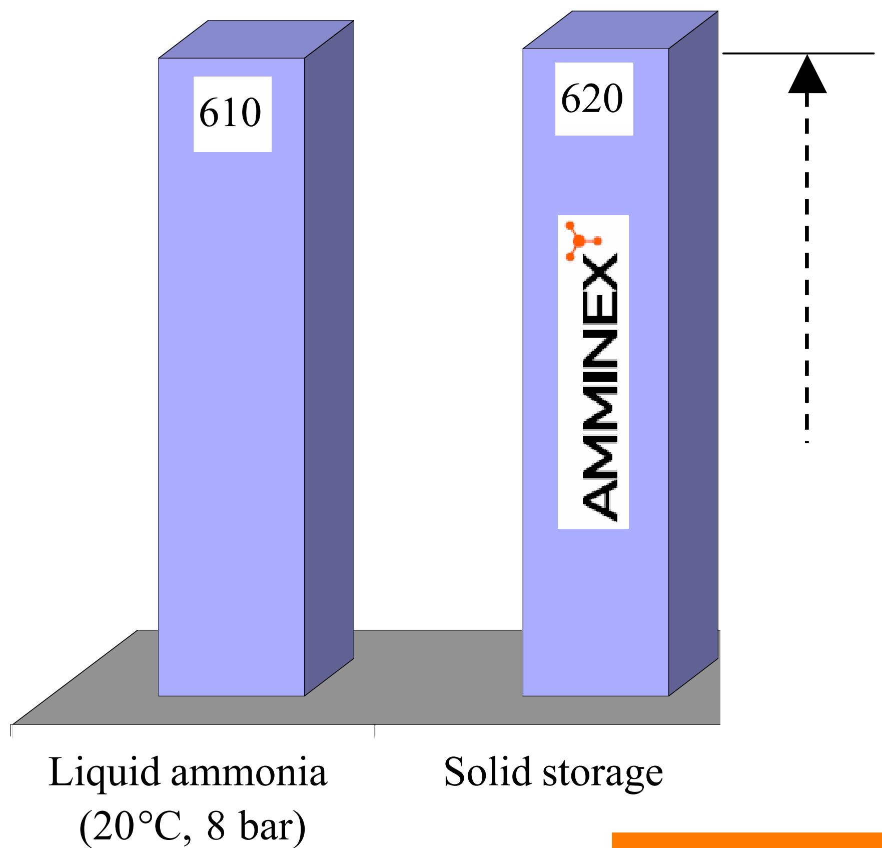
Ammonia Storage and Delivery system - ASDS





Overview of ammonia capacity

Ammonia capacity (measured in kg/m^3)

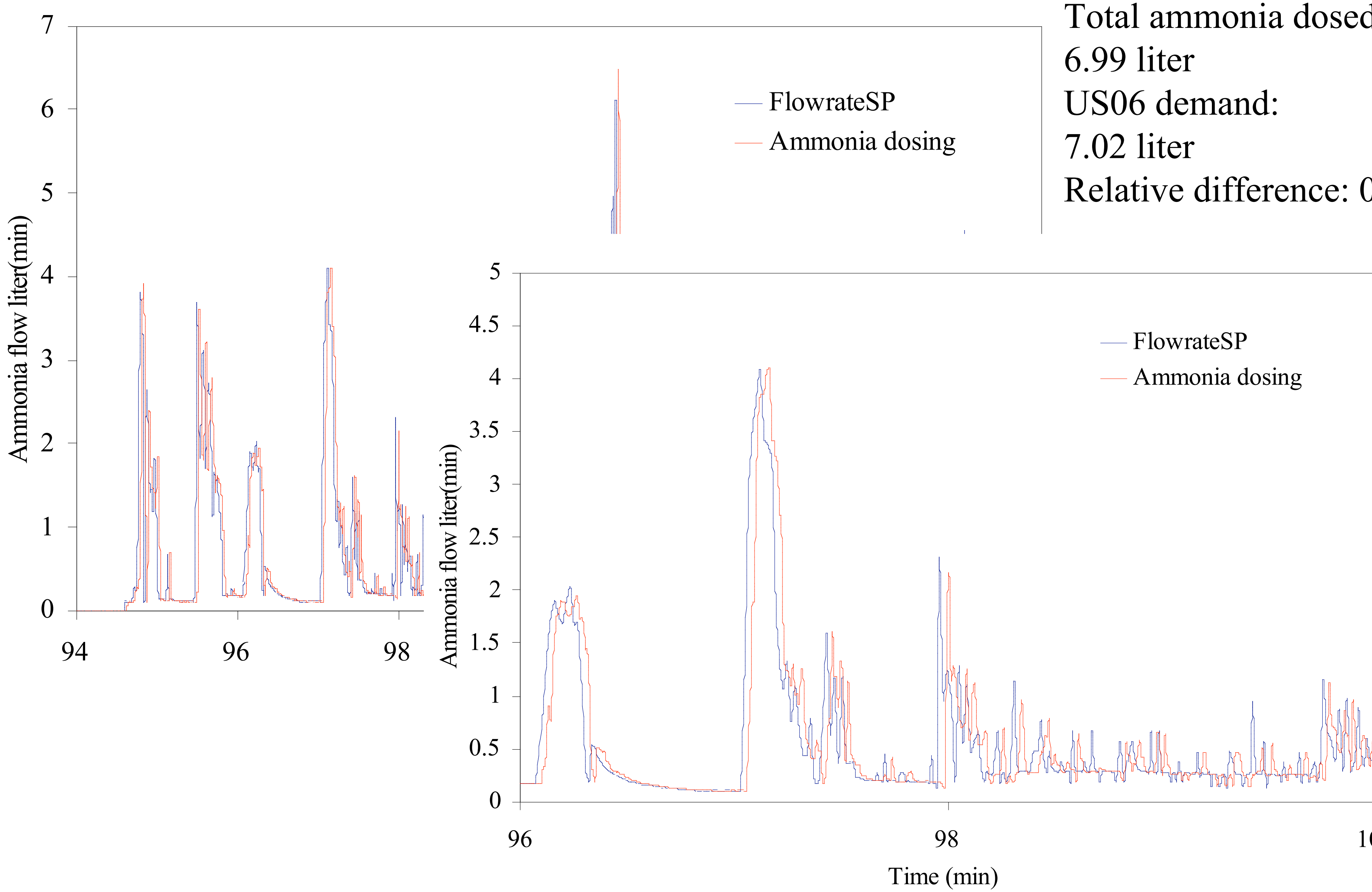


AdBlue:

3.1 times higher volume needed;
2.8 times higher mass needed

LD Service interval operation:
- **5kg NH_3 = 8 liter AdAmmine (~9.7kg)**
- **5kg NH_3 = 25 liter AdBlue (~27.4kg)**

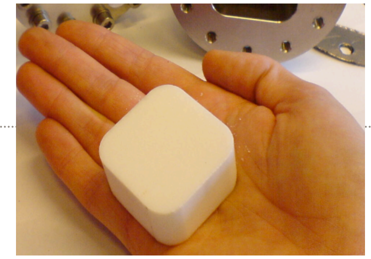
Dosing according to US06-cycle

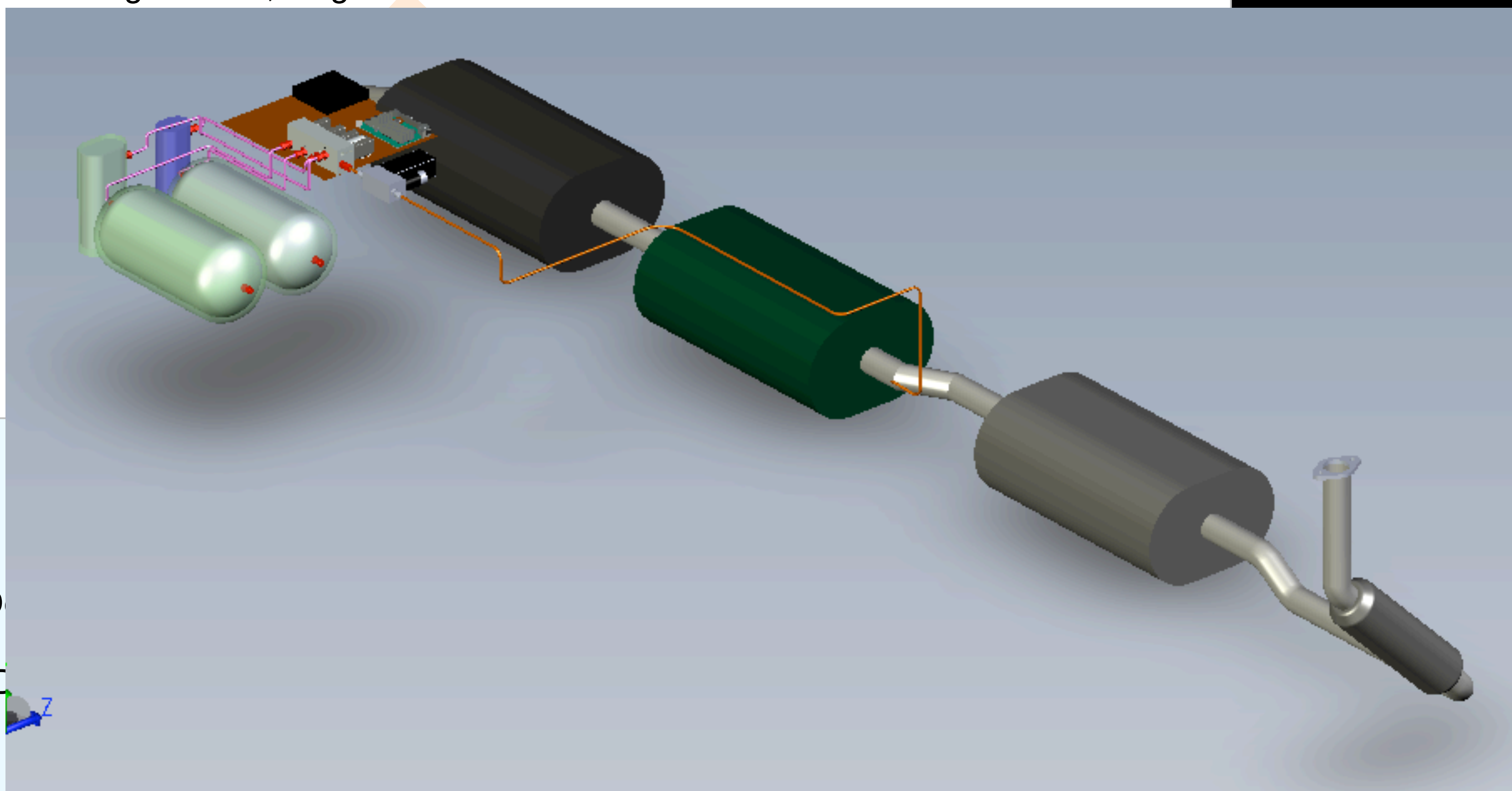


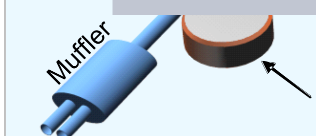
Total ammonia dosed:
6.99 liter
US06 demand:
7.02 liter
Relative difference: 0.5%

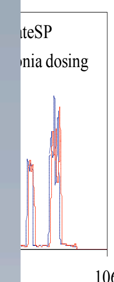
Ammonia stored safely in AdAmmine™:

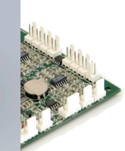
- "X"$(NH_3)_{6-8}Cl_2$ (>50 wt% NH_3; > 600g NH_3/liter)
- No degradation; long shelve life











Electronics and control:

- Algorithms for Power minimization
- OBD functions

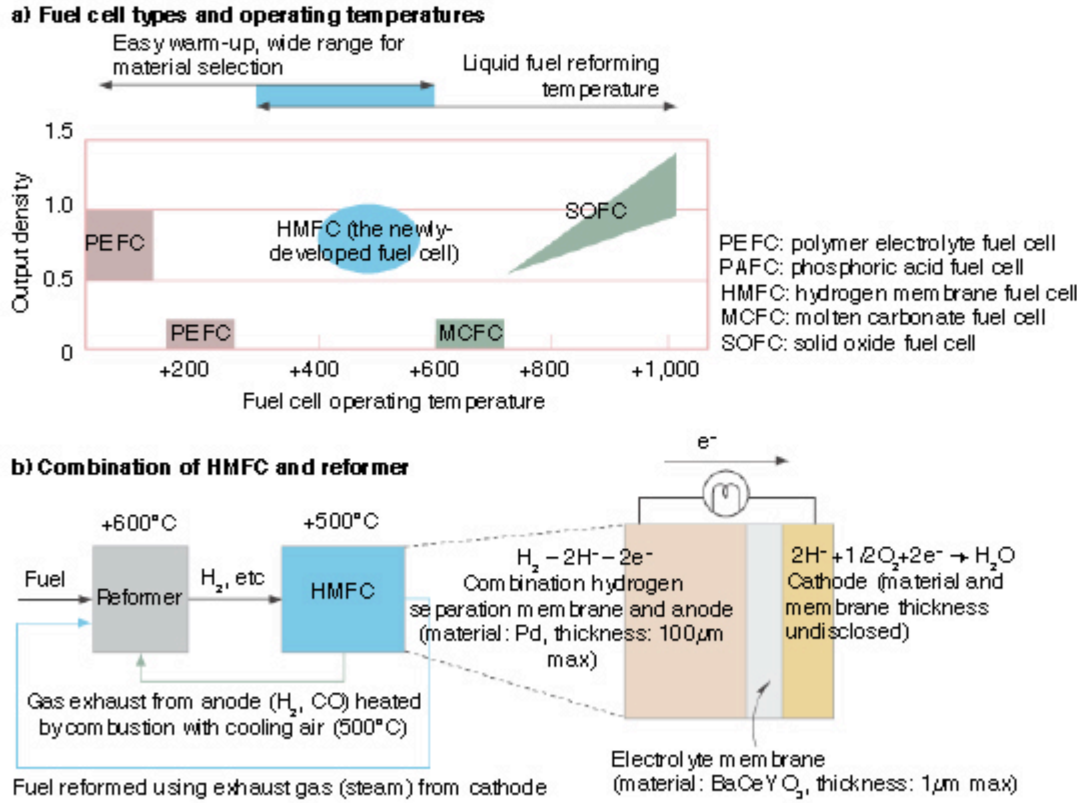
Summary

- Enabling ammonia for mass-market or end-user products within
  - Energy storage
  - NOx after treatment

- Thank you !

BACK-UP

Automotive initiatives with IT-FC



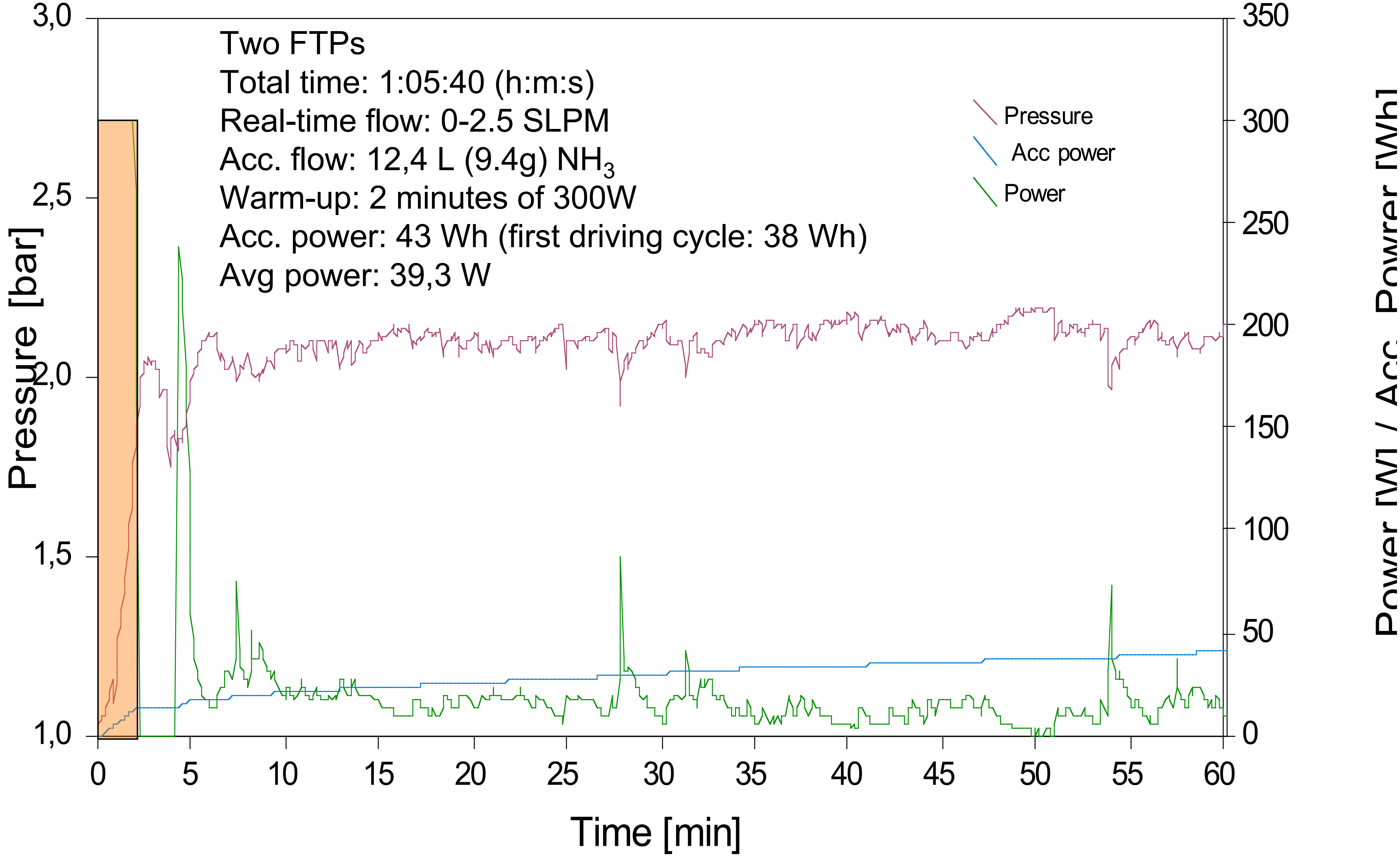
Toyota Develops Fuel Cell which Reforms Liquid Fuel (a) Fuel cell types and operating temperatures. HMFCs fulfill two key conditions at once: improved warm-up performance, and an operating temperature closer to the fuel reforming temperature. (b) Combination of HMFC and reformer. The unreacted H_2 and CO from the anode are combusted with O_2 (for cooling), providing the reformer with a heat source. H_20 (steam) from the cathode is used to reform the liquid fuel.

http://techon.nikkeibp.co.jp/NEA/archive/200408/322733/

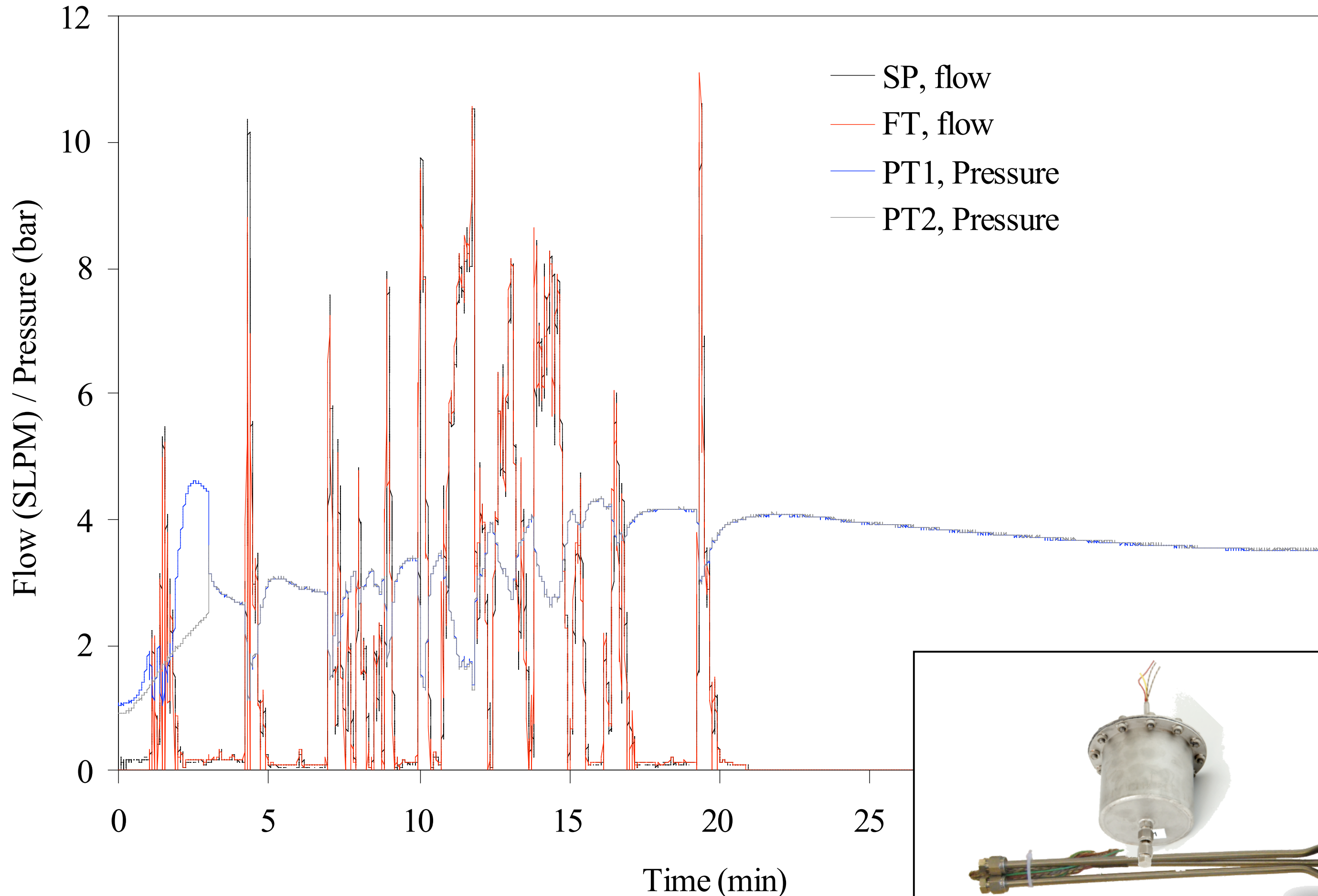
http://www.fuelcellsworks.com/Supppage714.html

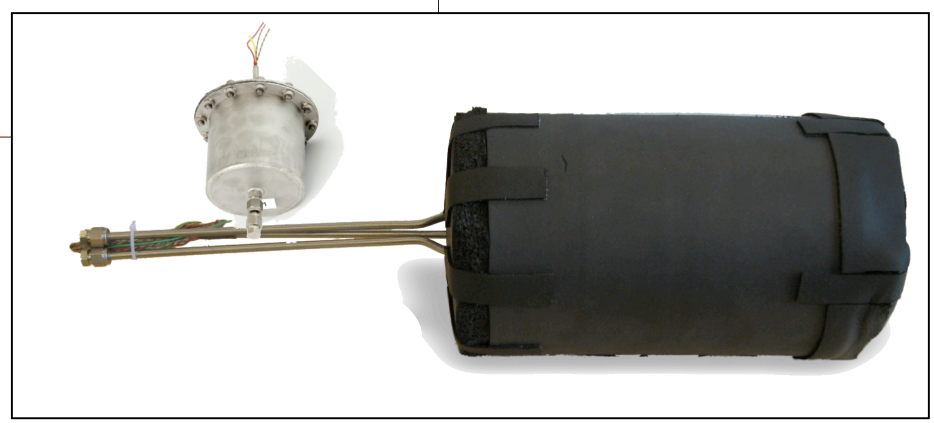
http://aiche.confex.com/aiche/s07/preliminaryprogram/abstract_81042.htm

4kg single unit

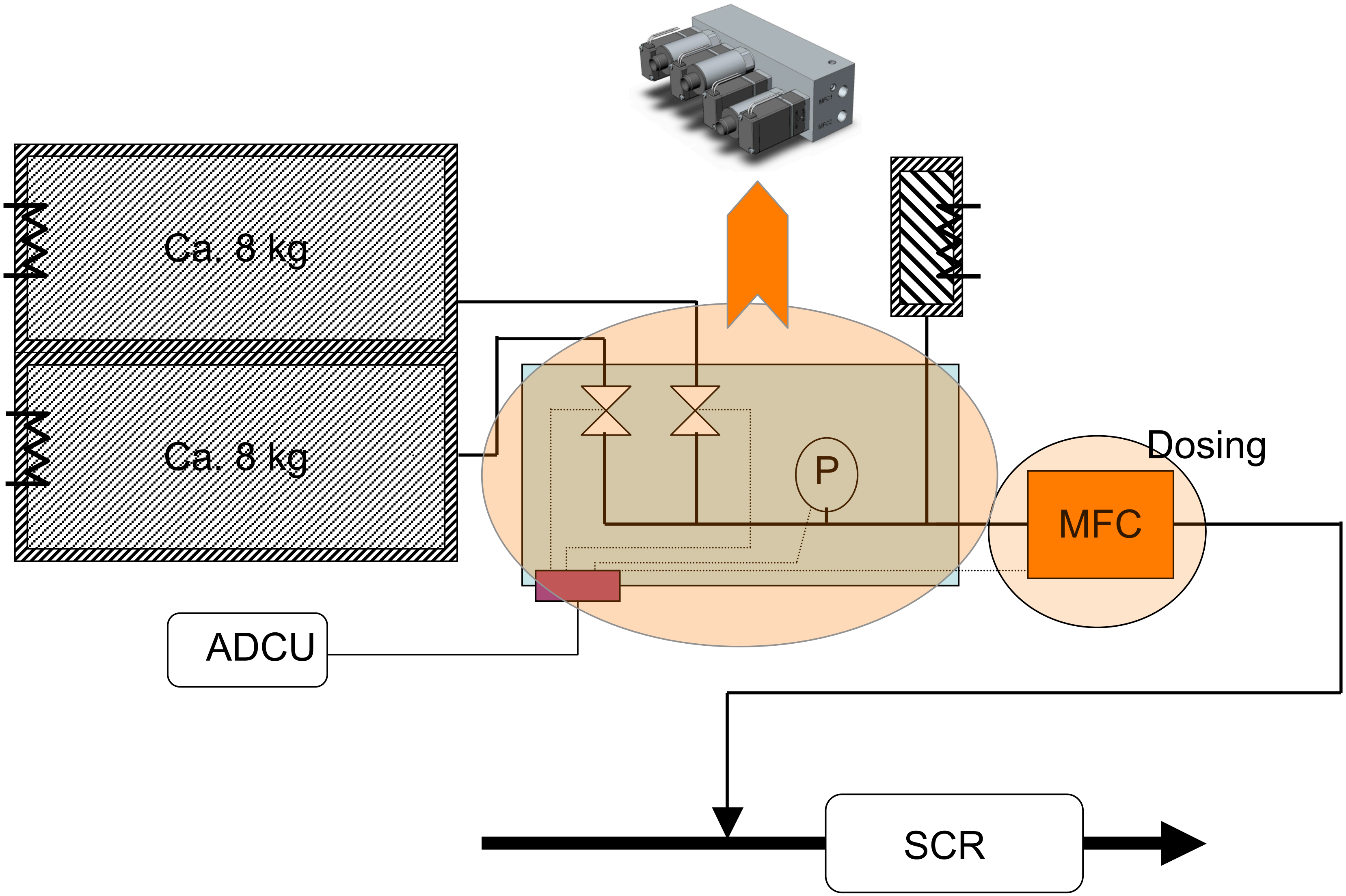


Demanding cold start with 4kg unit + 0.4kg start-up

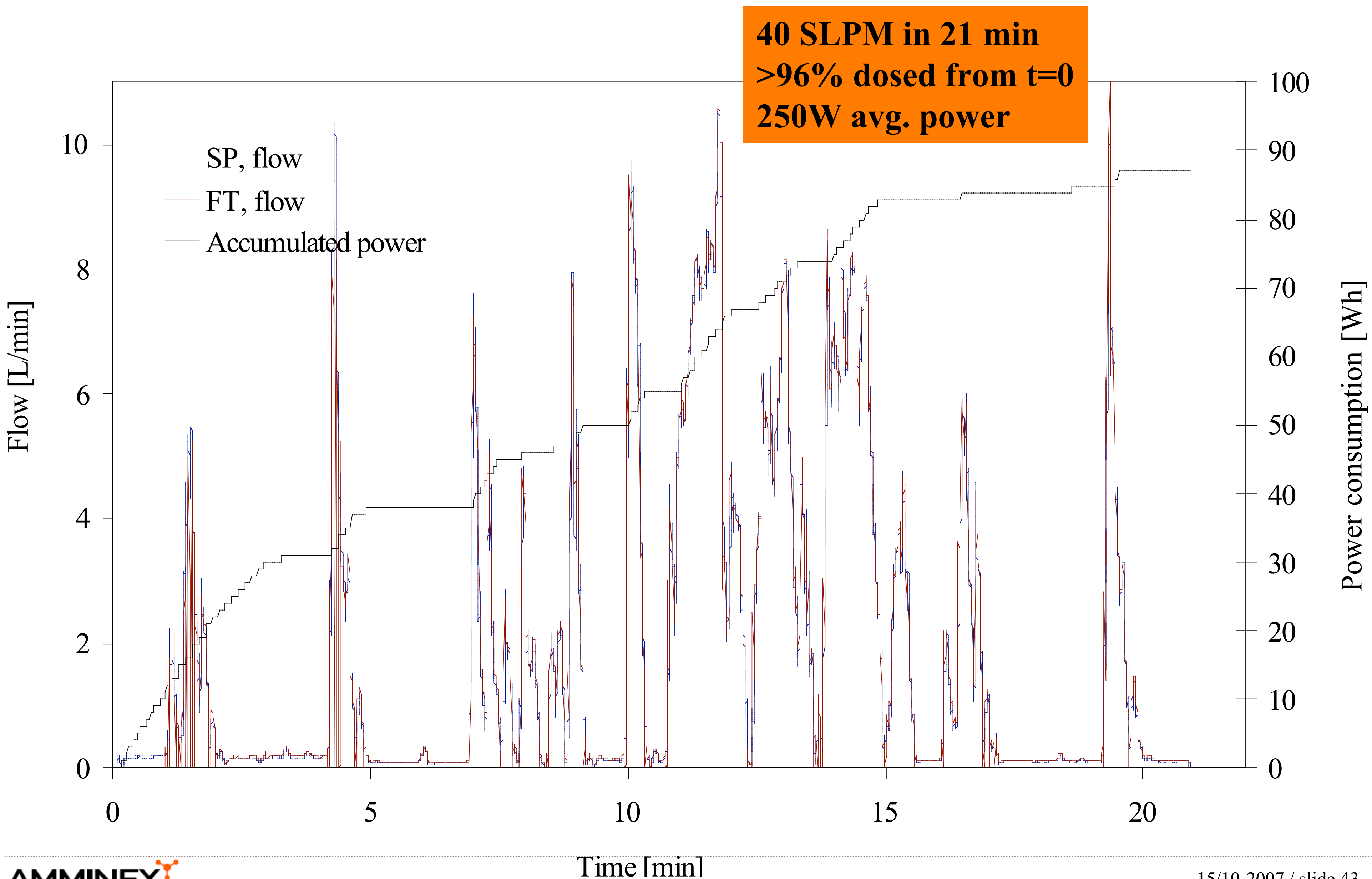




Full-sized system: Two replaceable cartridges



Dosing vs. power



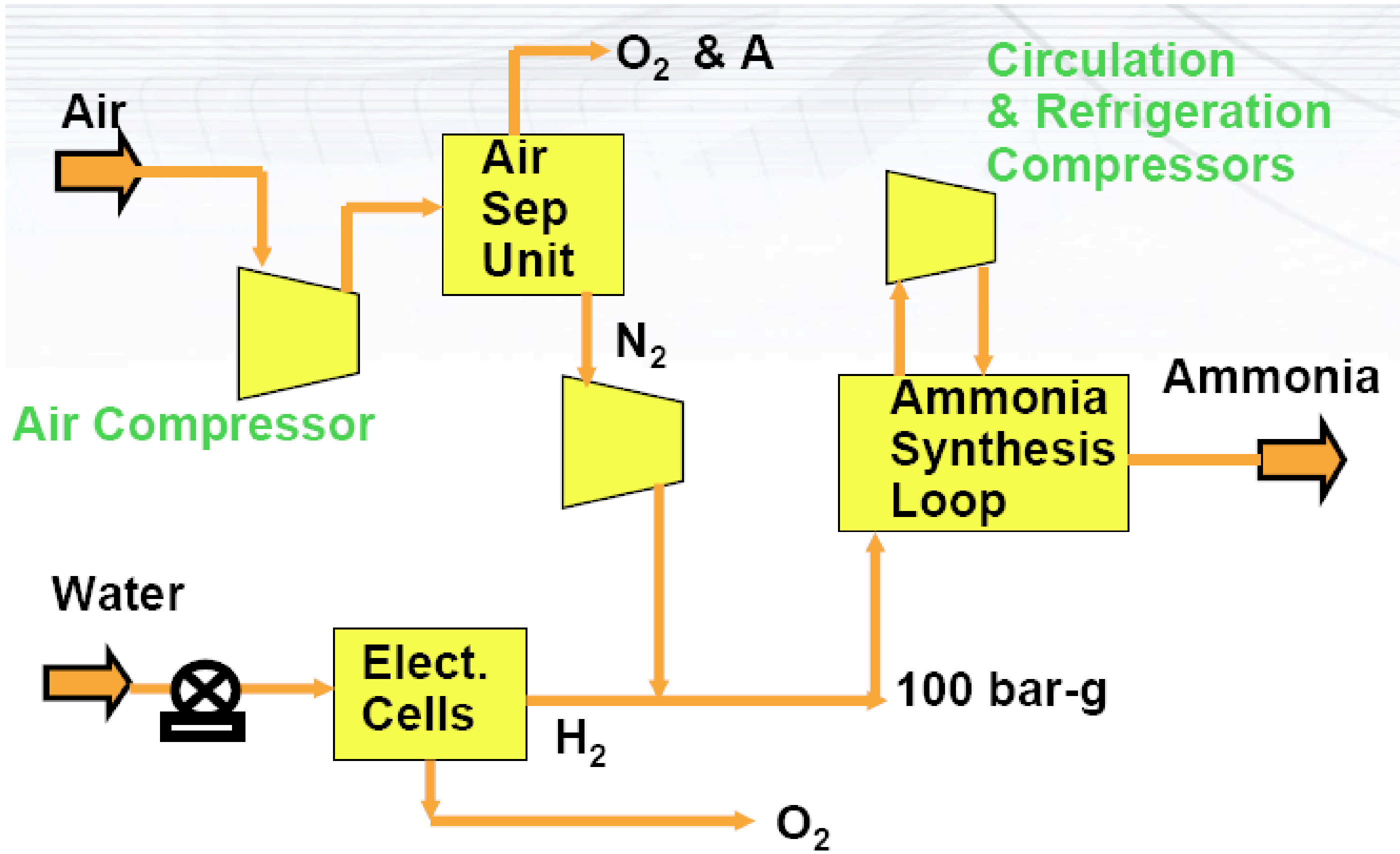
In-situ recharging of cartridges demonstrated

- Existing world-wide infrastructure for ammonia distribution
- Amminex has demonstrated that canisters can be recharged with storage material inside.

Example of some of the ammonia pipelines in US

[source: US DOE ammonia report].

Renewable ammonia synthesis



Metal ammine chemistry – the $MgCl_2$-NH_3 system

$$MgCl_2(s) + NH_3(g) \rightleftharpoons Mg(NH_3)Cl_2(s), \qquad \Delta H = 87.0\, kJ/mol\, NH_3$$

$$Mg(NH_3)Cl_2(s) + NH_3(g) \rightleftharpoons Mg(NH_3)_2Cl_2(s), \qquad \Delta H = 74.9\, kJ/mol\, NH_3$$

$$Mg(NH_3)_2Cl_2(s) + 4NH_3(g) \rightleftharpoons Mg(NH_3)_6Cl_2(s), \qquad \Delta H = 55.6\, kJ/mol\, NH_3$$

$$Average\ desorption\ enthalpy:\ 42.7 \frac{kJ}{mol\, H_2}$$

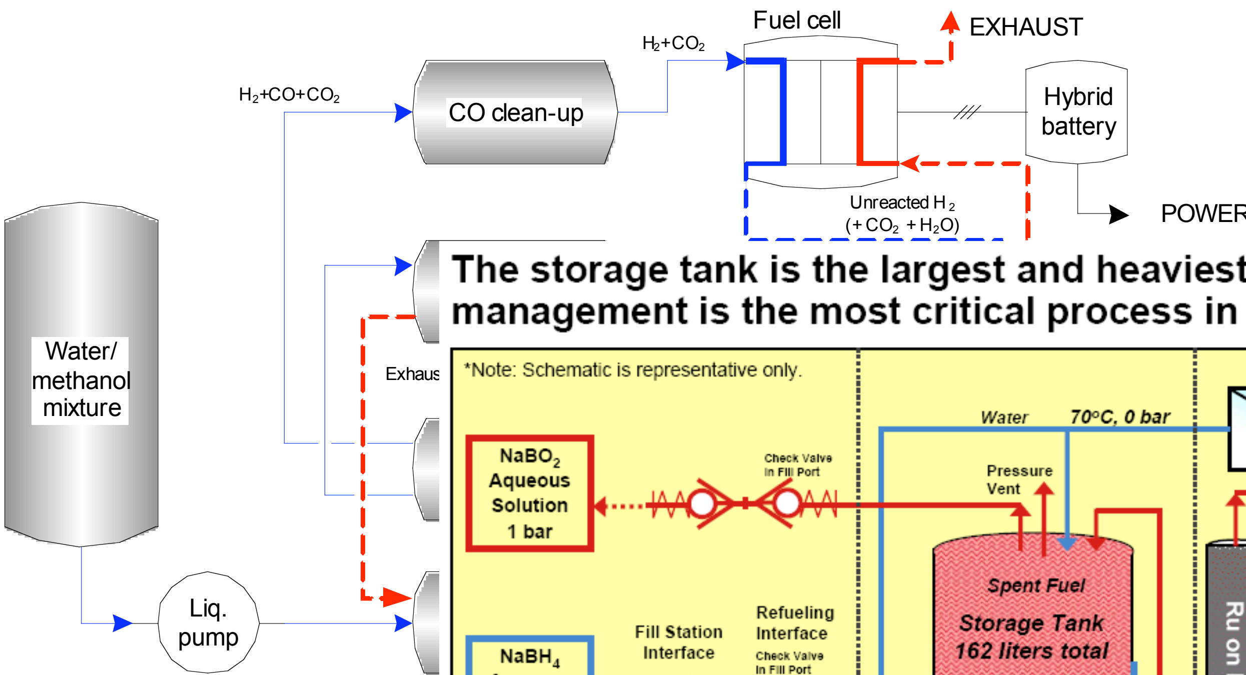
e.g., A. Werner, Nobel Prize Lecture “On the constitution and configuration of higher-order compounds”, 1913.

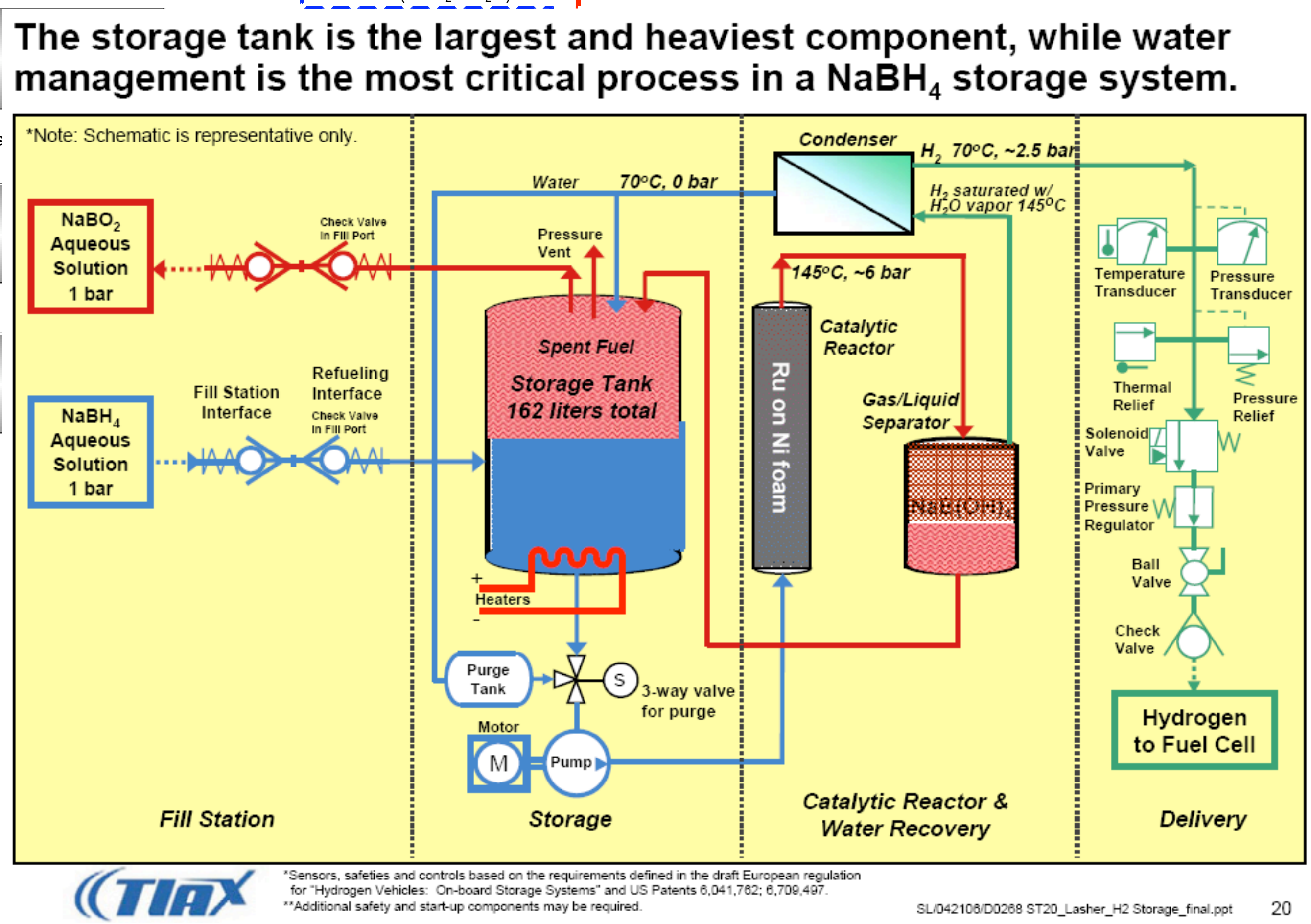
E. Lepinasse and B. Spinner, Rev. Int. Froid, 1994, 17, 309.

The ammonia content

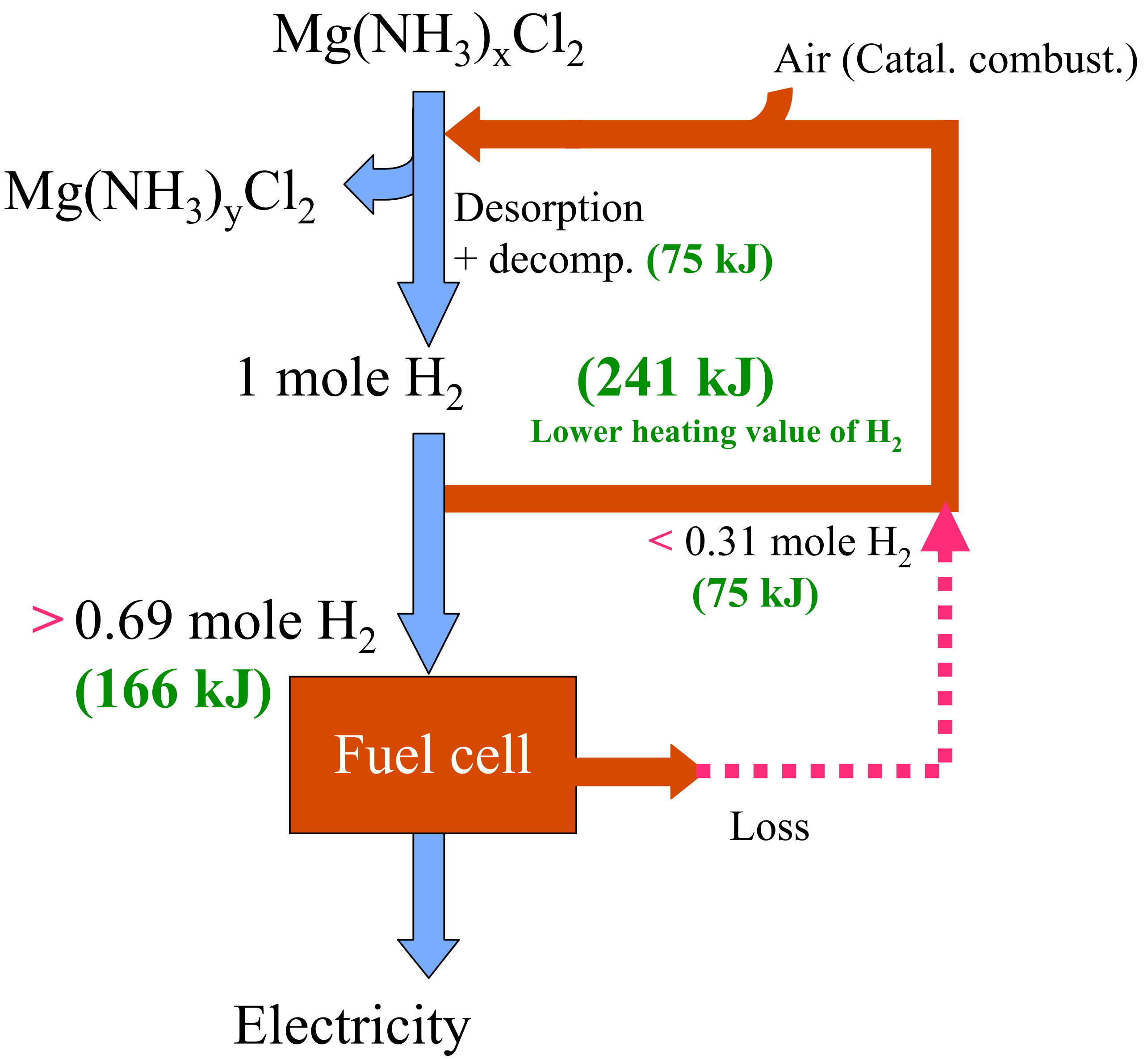
$Mg(NH_3)_6Cl_2$:	38.1 mol NH_3/l
Liquid ammonia:	40.1 mol NH_3/l

Comparison: Reformed methanol & Sod. Bo. Hyd.

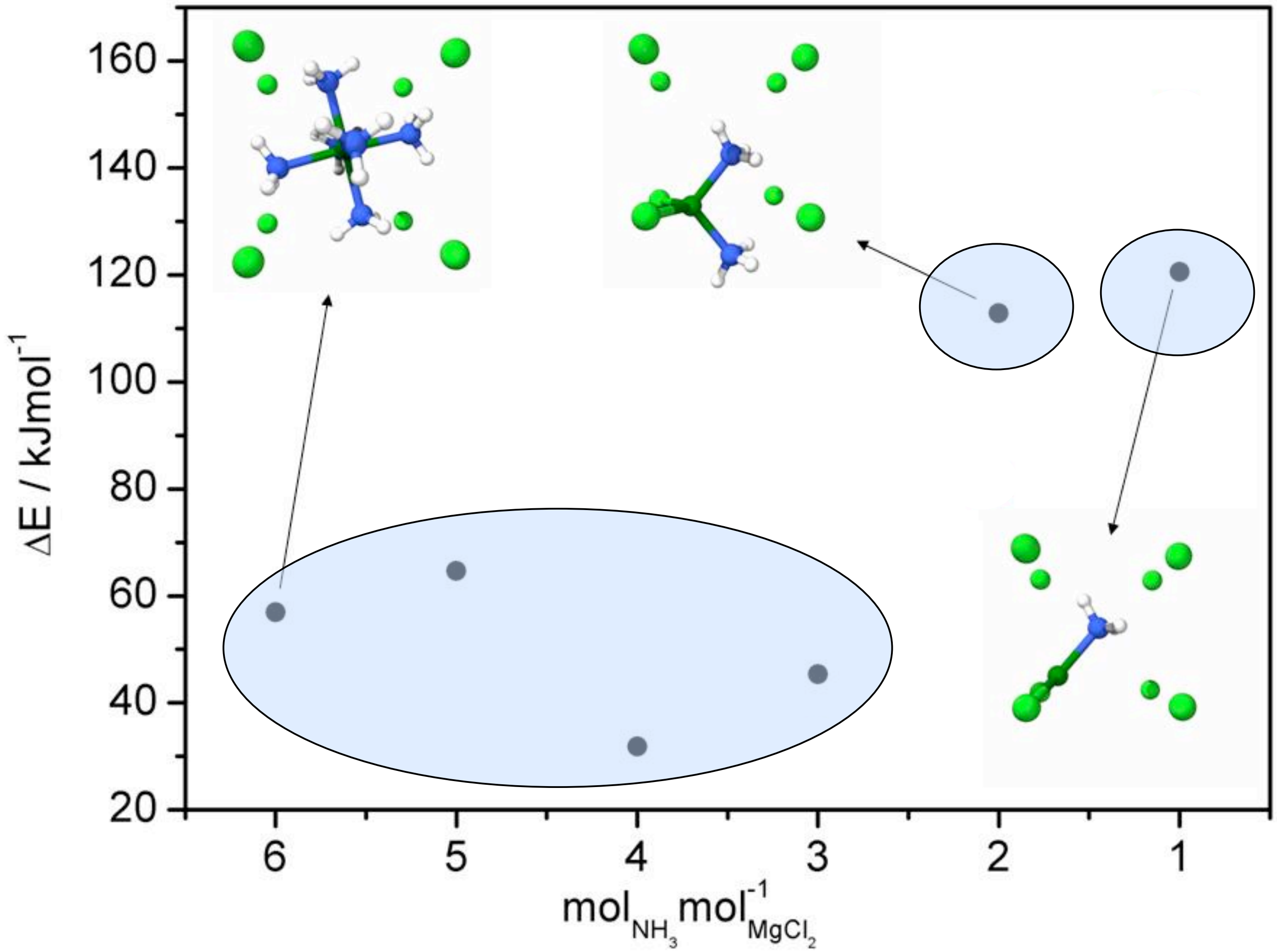




Heat integration – low temperature FC



Fundamental understanding of material properties



Hummelshøj, Sørensen, Kustova, Johannessen, Nørskov and Christensen,
J. Am. Chem. Soc., 2006