Electrochemical Synthesis of Ammonia in Solid Electrolyte Cells

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Ammonia Synthesis
(about 150 million tons/year)

$$N_2 + 3\,H_2 \Longleftrightarrow 2\,NH_3$$

- Conversion limited by thermodynamics. Conversion increases with P
- The reaction is exothermic (109 kJ/mol at 500^{o}C). Conversion decreases with T
- The triple N≡N bond. High T required for industrially acceptable reaction rates

The trade-off solution: **T = 430^{o} - 480^{o}C**
P = 150 - 250 bar
Fe (or Ru) - based catalysts
10-15 % conversion to NH_3

The main steps in the NH_3 synthesis plant

- Hydrogen production (highly endothermic)

  Methane steam reforming: $CH_4 + H_2O \rightarrow CO + 3\,H_2$

  Water gas shift: $CO + H_2O \rightarrow CO_2 + H_2$
- Preparation of synthesis gas (extreme purification)
- Pressurization (150-250 bar)
- Ammonia synthesis (exothermic): $N_2 + 3H_2 \rightarrow 2\,NH_3$

Overall Reaction:

$$3\,CH_4 + 6\,H_2O + 4\,N_2 \Longleftrightarrow 3\,CO_2 + 8\,NH_3$$

In industrial practice, the CO_2/NH_3 molar ratio is about 1.1 (instead of 0.4)

Plants convert N_2 to NH_3 at ambient conditions:

N_2 + 6 H^+ + 6e^- (nitrogenase) ➔ 2NH_3

NH_3 synthesis was studied at ambient conditions in liquid electrolytes*.

BUT

* E.E. van Tamelen, B. Akermark, J. Amer. Chem. Soc. 90 (1968) 4492.
A.V. Gorodiskii, et al, React. Kinet. Catal. Lett. 11 (1979) 337.
A. Sclafani, V. Augugliano, M. Schiavello, J. Electrochem. Soc. 130 (1983) 734.
M. Halmann, J. Electroanal. Chem. 181 (1984) 307.
C.J. Pickett J. Talarmin, Mature, 317, (1985) pp. 652-653
N. Furuya, H. Yoshiba, J. Electroanal. Chem. 272 (1989) 263-266.
A. Tsuneto, A. Kudo, T. Sakata, Chem. Lett. Jpn. (1993) 851.
G.J. Leigh, Science, 268 (1995) 827.

Success, was limited:

liquid electrolytes operate at low temperatures where reaction kinetics are too slow.

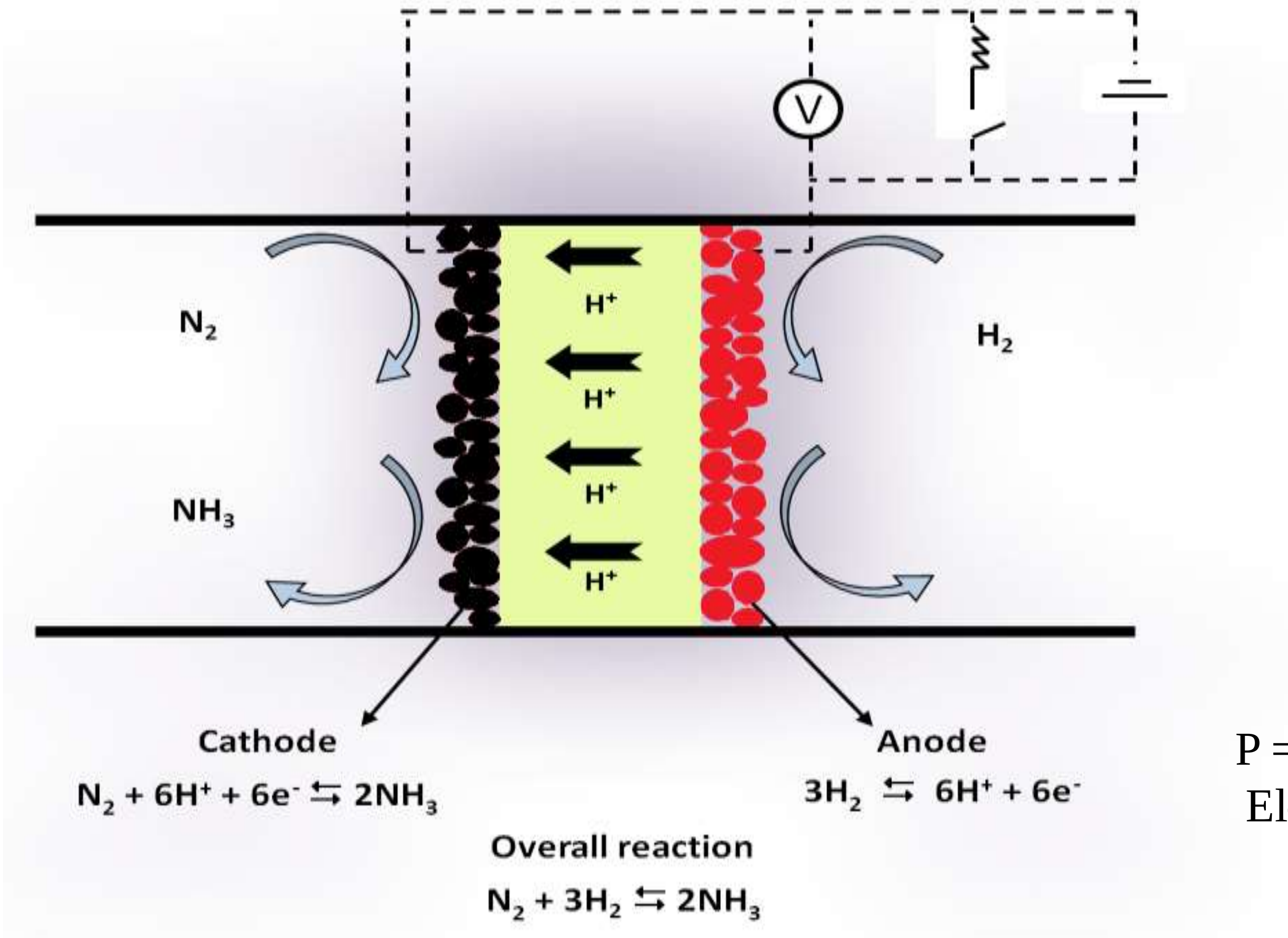
1981* : Discoveryof high temperature solid state proton (H+) conductors

Examples of Solid Electrolyte Materials (Perovskites) :

$SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ $SrCe_{0.95}Y_{0.05}O_{3-\delta}$ $SrZr_{0.90}Y_{0.10}O_{3-\delta}$

*** H. Iwahara, et al, Solid State Ionics 4, 359–363 (1981).**

Solid State Ammonia Synthesis (SSAS)

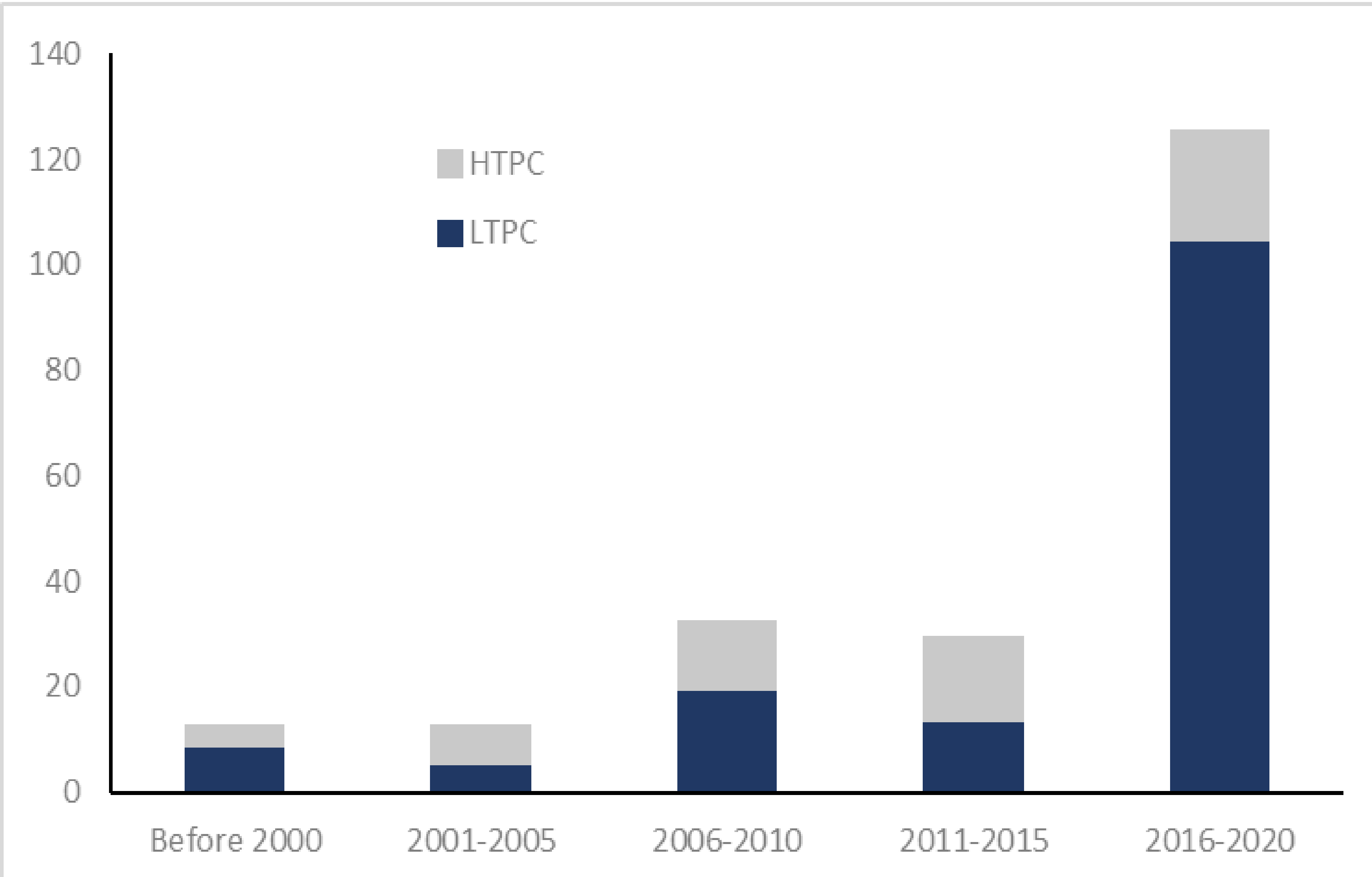


P = 1 bar, T = 570°C,

Electrolyte: $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$

G. Marnellos, M. Stoukides , Science, 282, 95–98 (1998).

Studies on the Electrochemical Synthesis of Ammonia



The two major problems

SOLID ELECTROLYTE: High Proton (H^+) Conductivity

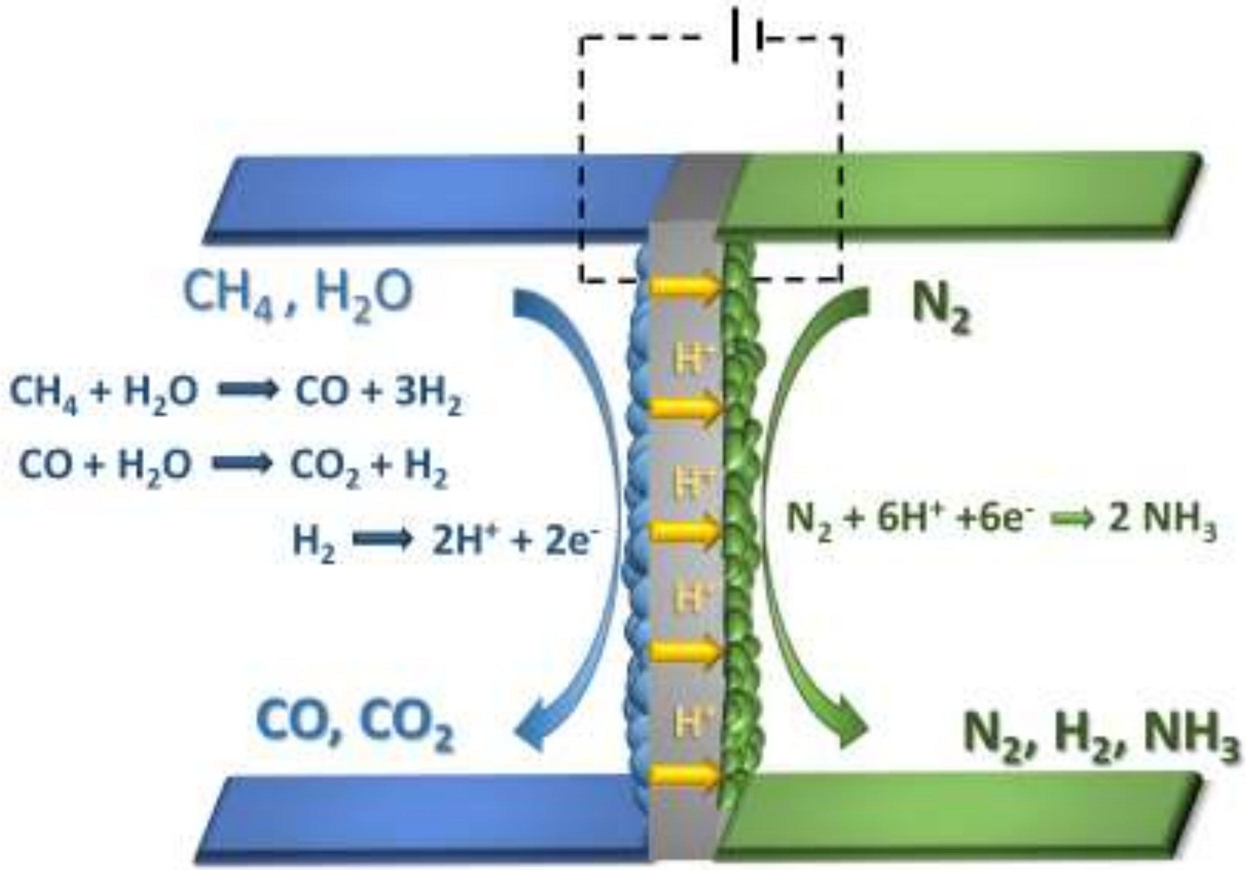
Production rate is limited by the H^+ Flux

CATHODIC ELECTRODE: High Faradaic Efficiency

Desired reaction: $1/2\ N_2 + 3\ H^+ + 3\ e^- \Longrightarrow NH_3$

Competing reaction: $2\ H^+ + 2\ e^- \Longrightarrow H_2$

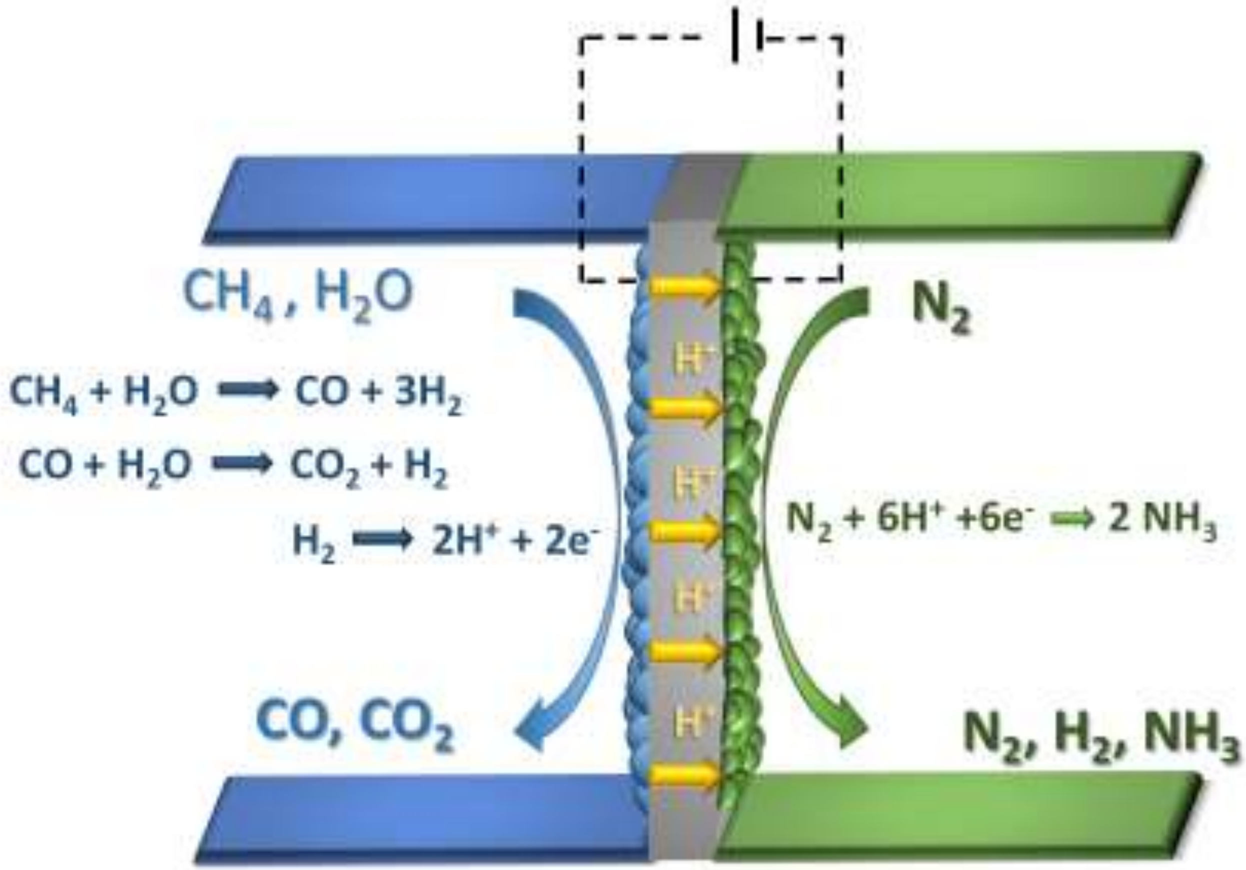
Combined SSAS synthesis and CH_4-H_2O reforming



Overall: $3 CH_4 + 6 H_2O + 4 N_2 \rightarrow 8 NH_3 + 3 CO_2$

- Methane conversion increases by H_2 removal (operation at lower T)
- Purification of hydrogen is eliminated
- The high Pressure requirement is reversed: $N_2 \rightarrow 2 NH_3$

Combined SSAS synthesis and CH_4-H_2O reforming



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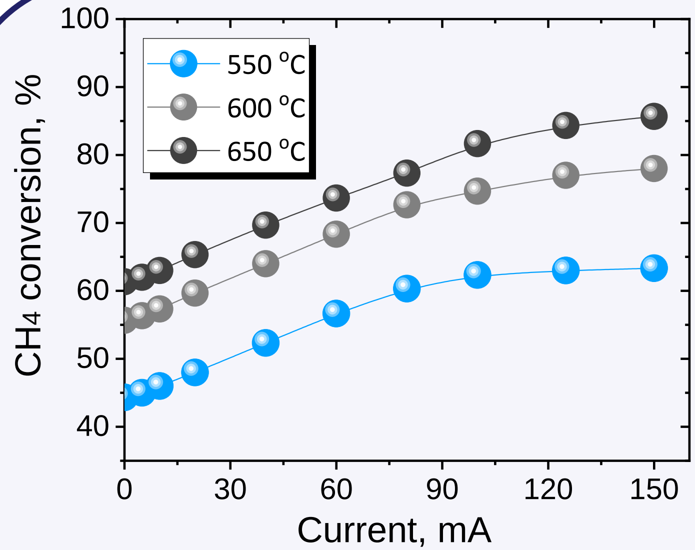
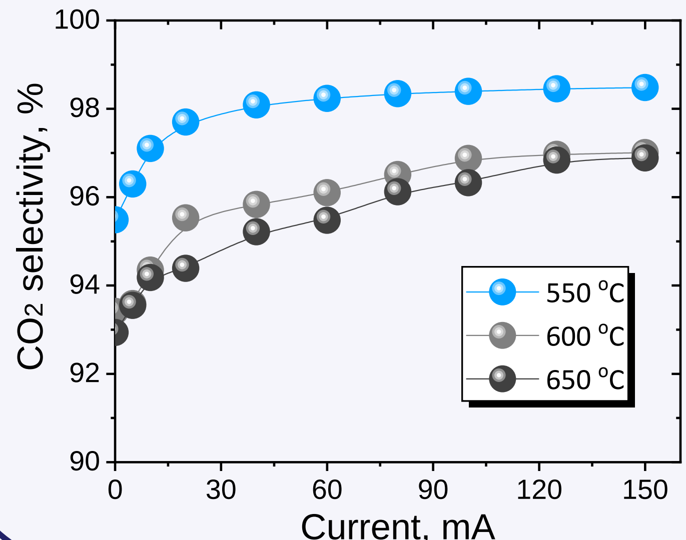
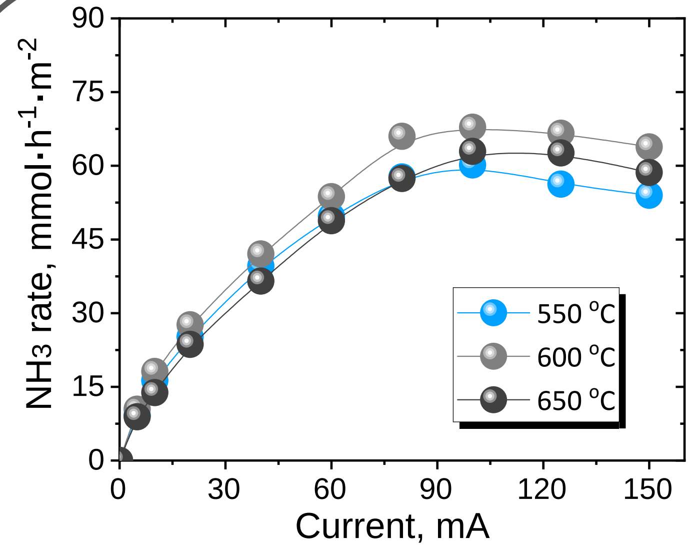
Results of the combined process

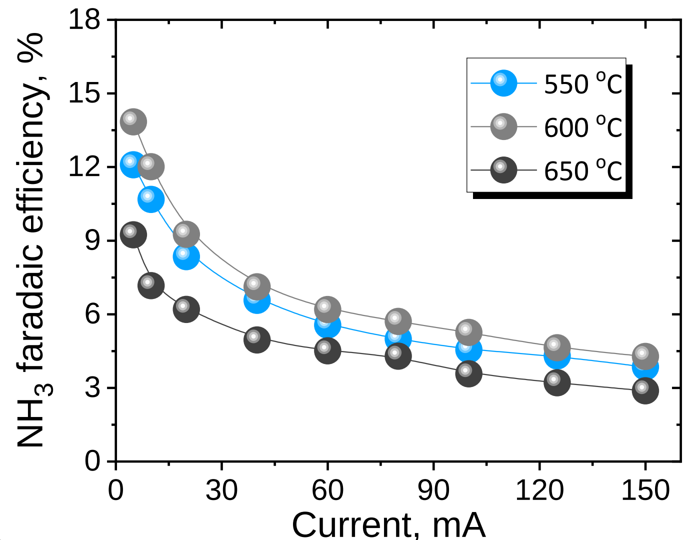
Anode side





Cathode side





Summary of Experimental Results

At the anode:

methane conversion up to 70%

CO_2 selectivity > 99%.

At the cathode:

NH_3 is formed at a rate of up to 1.95×10^{-9} $mol \cdot s^{-1} \cdot cm^{-2}$

Corresponding Faradaic Efficiency of 5.5%.

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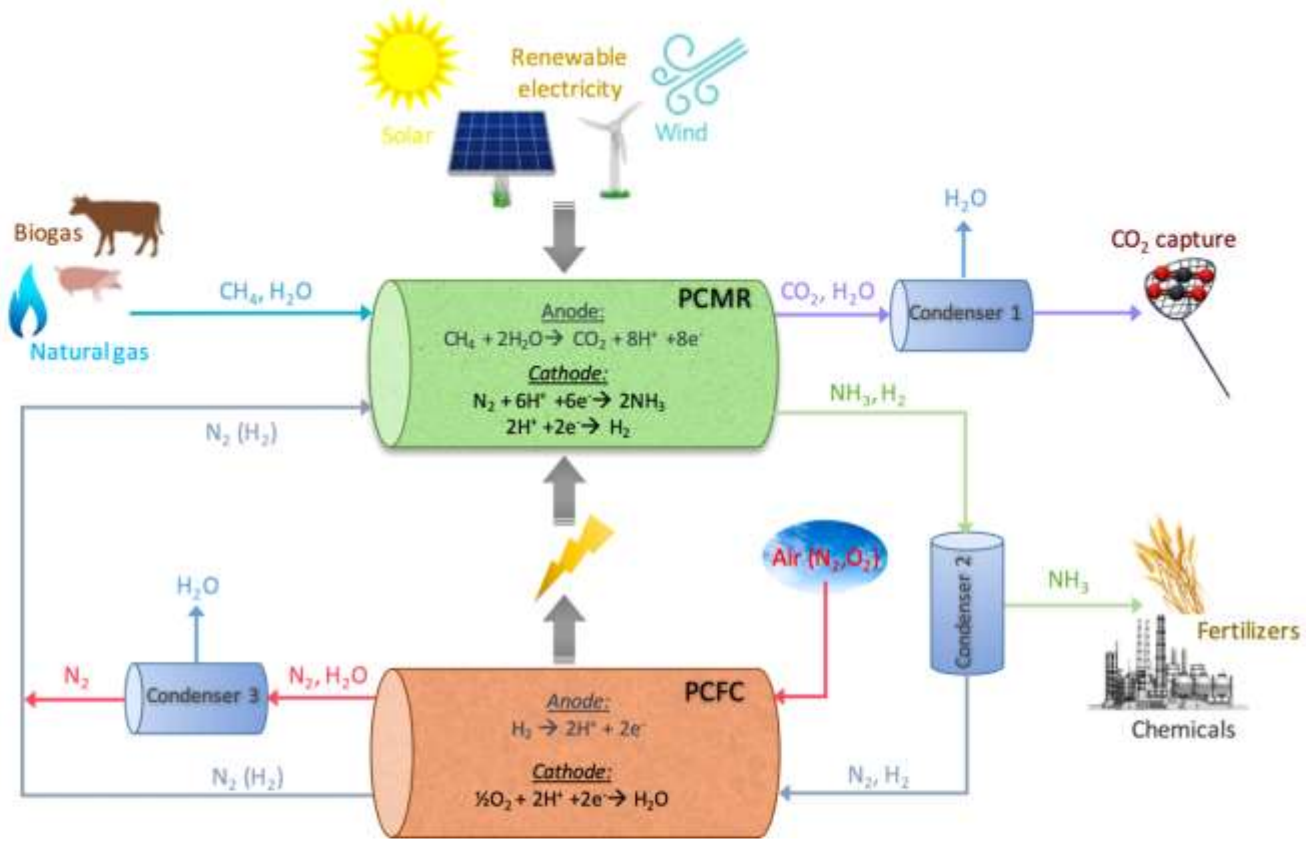
Visualizing an electrochemical HB



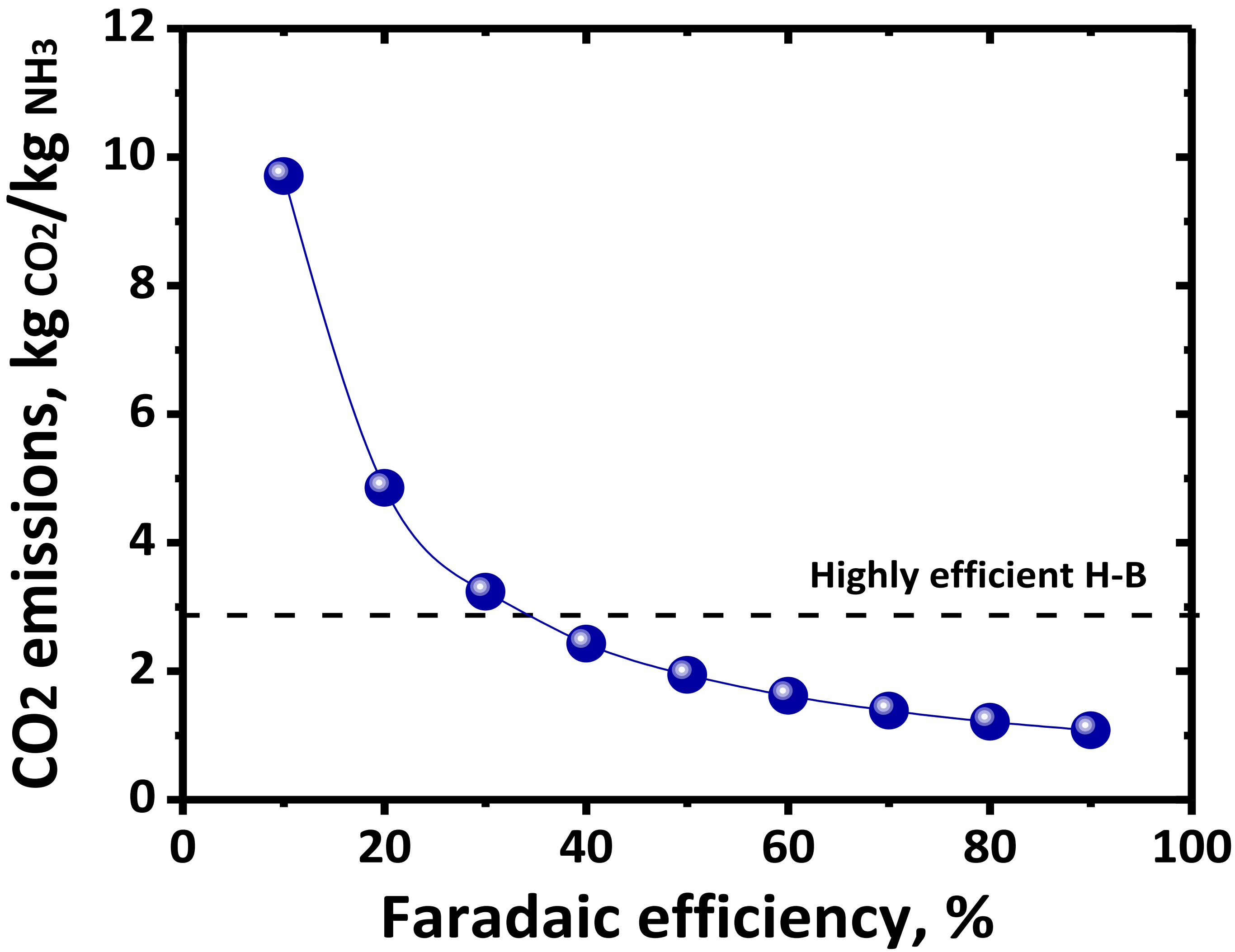
SSAS Reactor: $CH_4 + H_2O \iff CO_2 + 6\,H^+ + 6e^-$ (anode)

$N_2 + 6\,H^+ + 6\,e^- \iff 2\,NH_3$ (cathode)

PCFC Reactor: $H_2 \iff 2\,H^+ + 2\,e^-$ (anode)

$1/2\,O_2 + 2\,H^+ + 2\,e^- \iff H_2O$ (cathode)

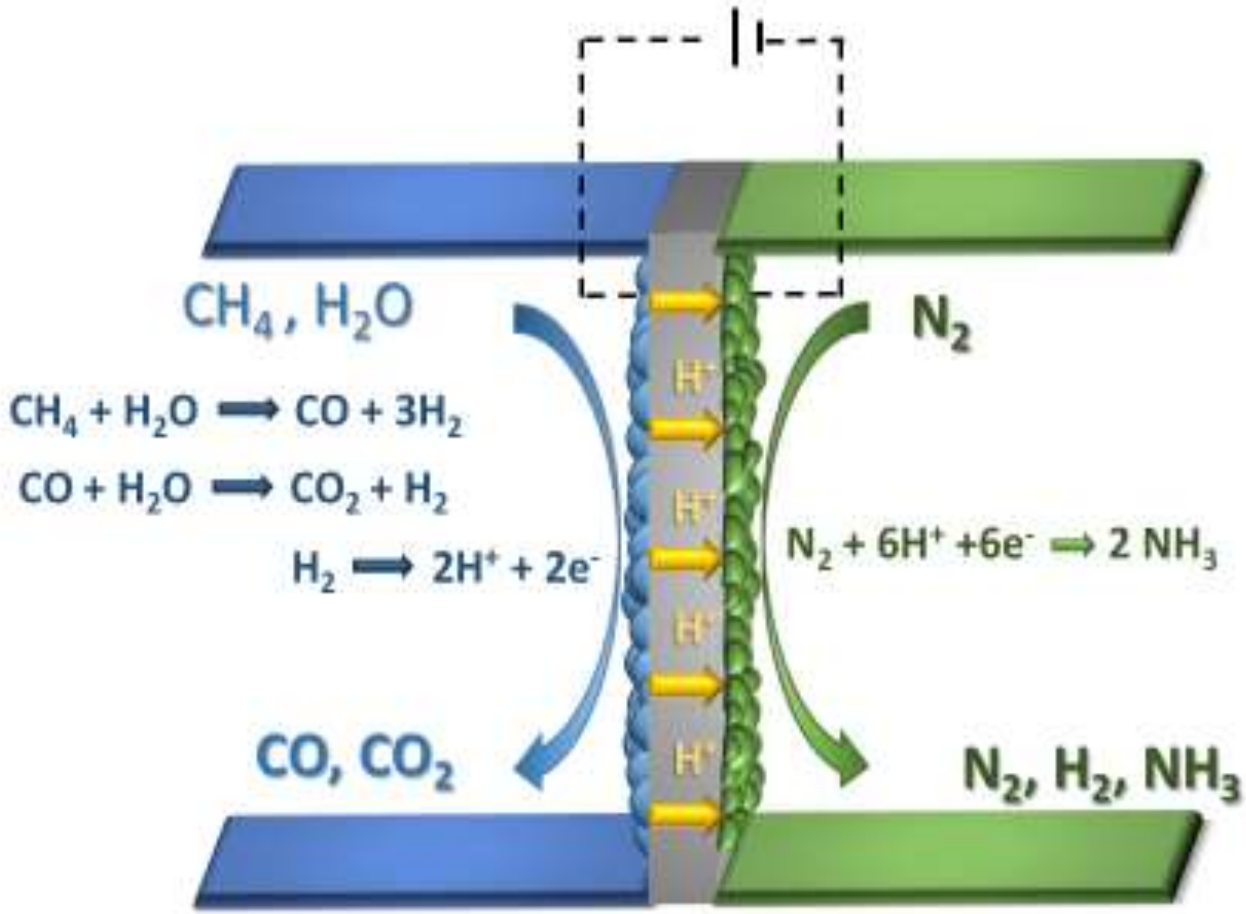
(The PCFC is assumed to operate at a 45% efficiency)



CO2 emissions, kg CO2/kg NH3
Faradaic efficiency, %
Highly efficient H-B
0
2
4
6
8
10
12
0
20
40
60
80
100

DECARBONIZATION??

Combined SSAS synthesis and CH_4-H_2O reforming



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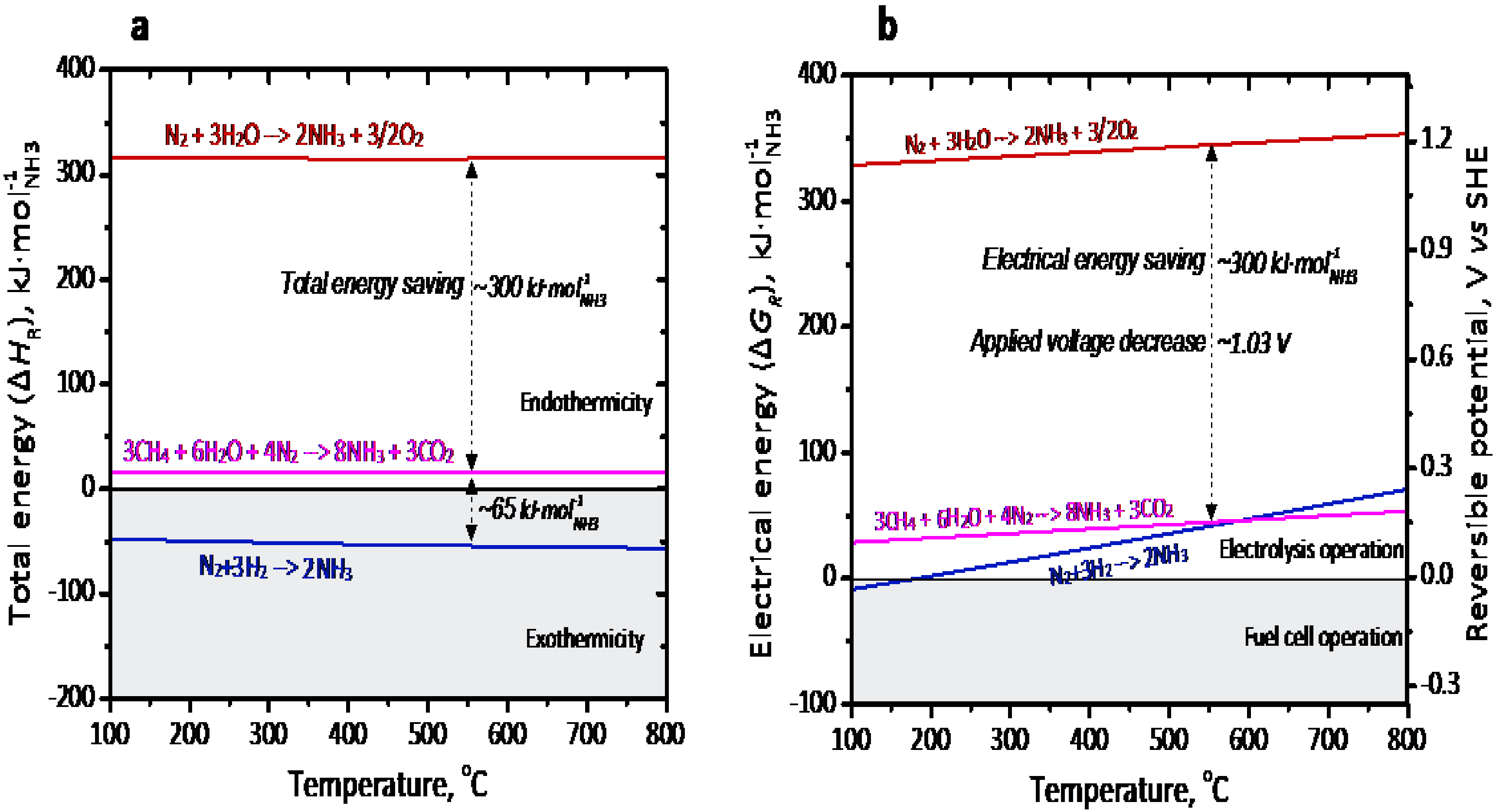

a
Total energy (ΔH_R), kJ·mol⁻¹_NH3
N2 + 3H2O --> 2NH3 + 3/2O2
Total energy saving ~300 kJ·mol⁻¹NH3
Endothermicity
3CH4 + 6H2O + 4N2 --> 8NH3 + 3CO2
~65 kJ·mol⁻¹NH3
N2+3H2 --> 2NH3
Exothermicity
Temperature, °C
b
Electrical energy (ΔG_R), kJ·mol⁻¹_NH3
Reversible potential, V vs SHE
N2 + 3H2O --> 2NH3 + 3/2O2
Electrical energy saving ~300 kJ·mol⁻¹NH3
Applied voltage decrease ~1.03 V
3CH4 + 6H2O + 4N2 --> 8NH3 + 3CO2
N2+3H2 --> 2NH3
Electrolysis operation
Fuel cell operation
Temperature, °C

Thank for your attention