An Electrochemical Haber-Bosch Process*

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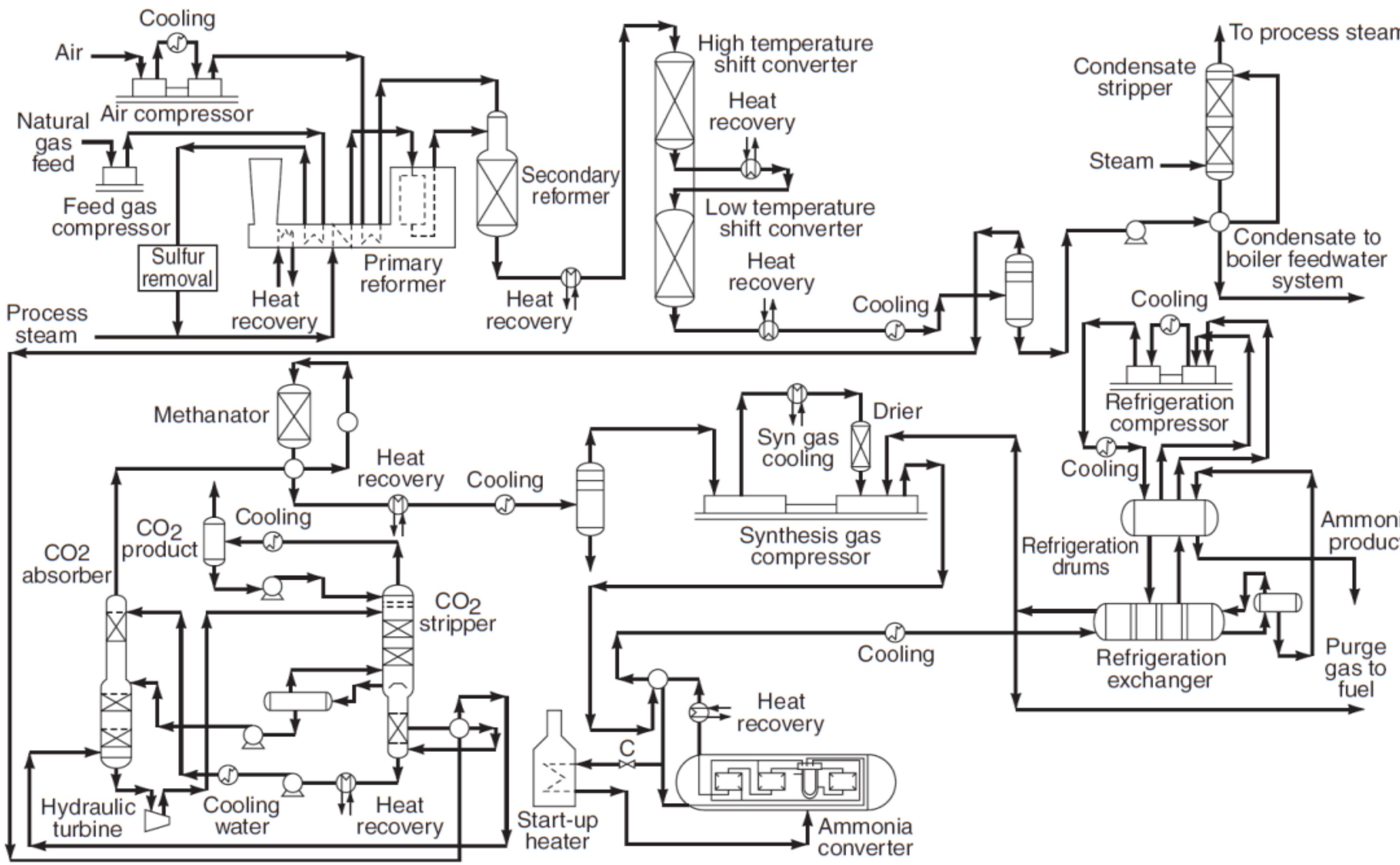
* *JOULE, 4(1)pp. 142-158 (2020).*

Industrial Ammonia Production



- Supports >50% of earth's population
- High T, P → High capital cost
- Responsible for 1-2% energy consumption and CO_2 emissions worldwide

T. Eggeman, in "Kirk- Othmer Encyclopedia of Chemical Technology," 4th edition, John Wiley (2008)

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:

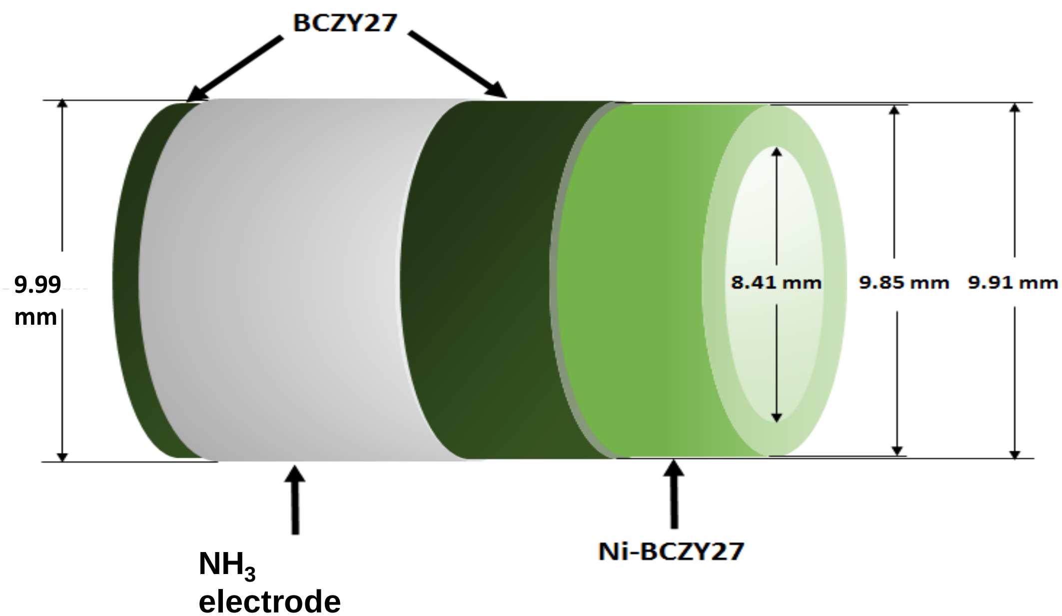
$$3\ CH_4 + 6\ H_2O + 4\ N_2 \Longleftrightarrow 3\ CO_2 + 8\ NH_3$$

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

Plants and bacteria produce NH_3 at ambient conditions (nitrogenase, N_2 , H^+, e^-)

Discovery* and development of high temperature H^+ conductors

Development * * of ceramic membrane reactors with high H^+ conductivity



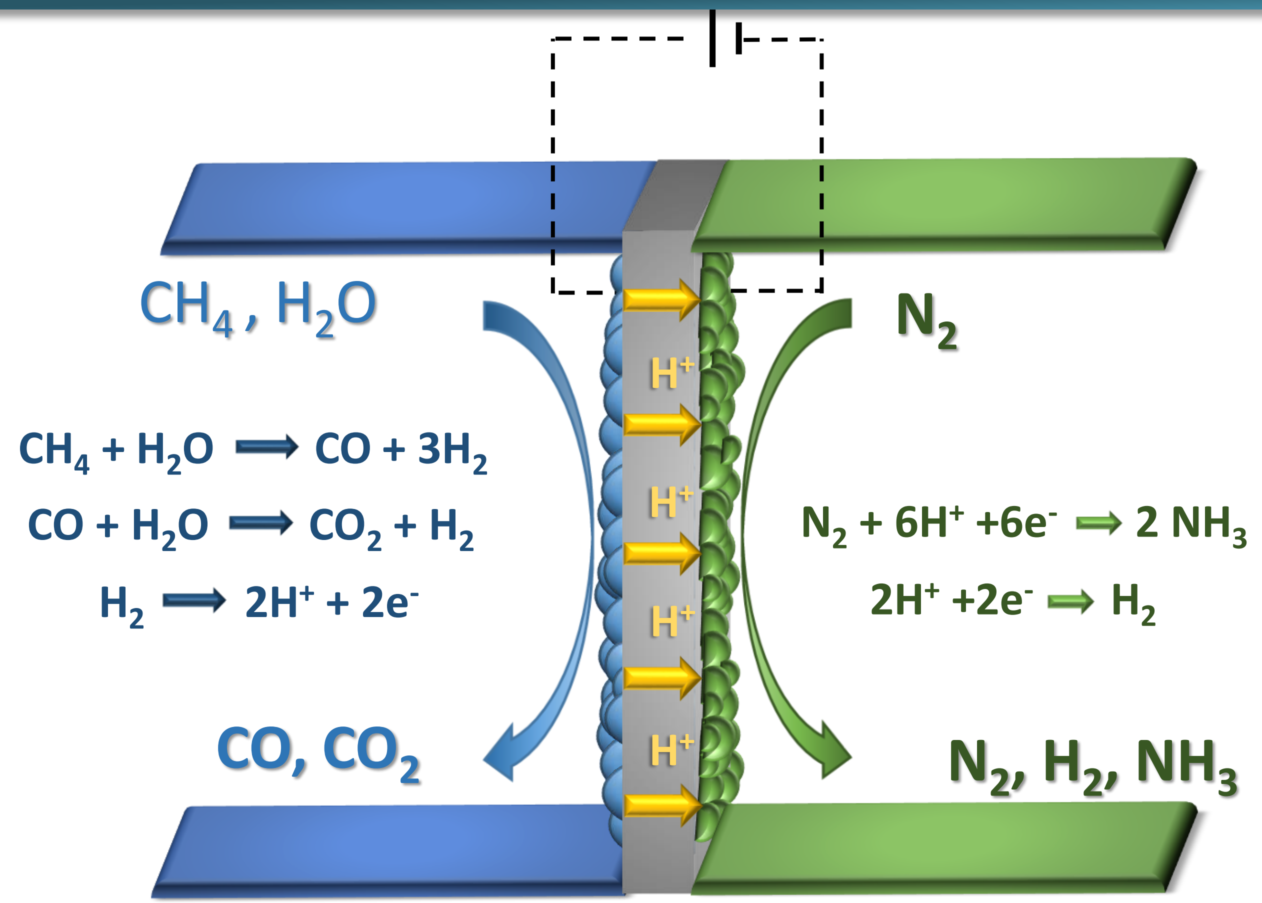
- ✓ High H^+ conductivity (10^{-6} moles H_2 cm^{-2} s^{-1}) at 450-700 °C
- ✓ The hydrogen source can be a hydrocarbon (e.g. steam reforming)

Electrolyte:	**$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{2.9}$ (BZCY72), thickness: 30 µm**
Counter Electrode:	**Ni-BZCY72, area: 20-25 cm^{-2}**
Working Electrode:	**VN-Fe, area : 8 cm^{-2}**
Tube length:	**250 mm**

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

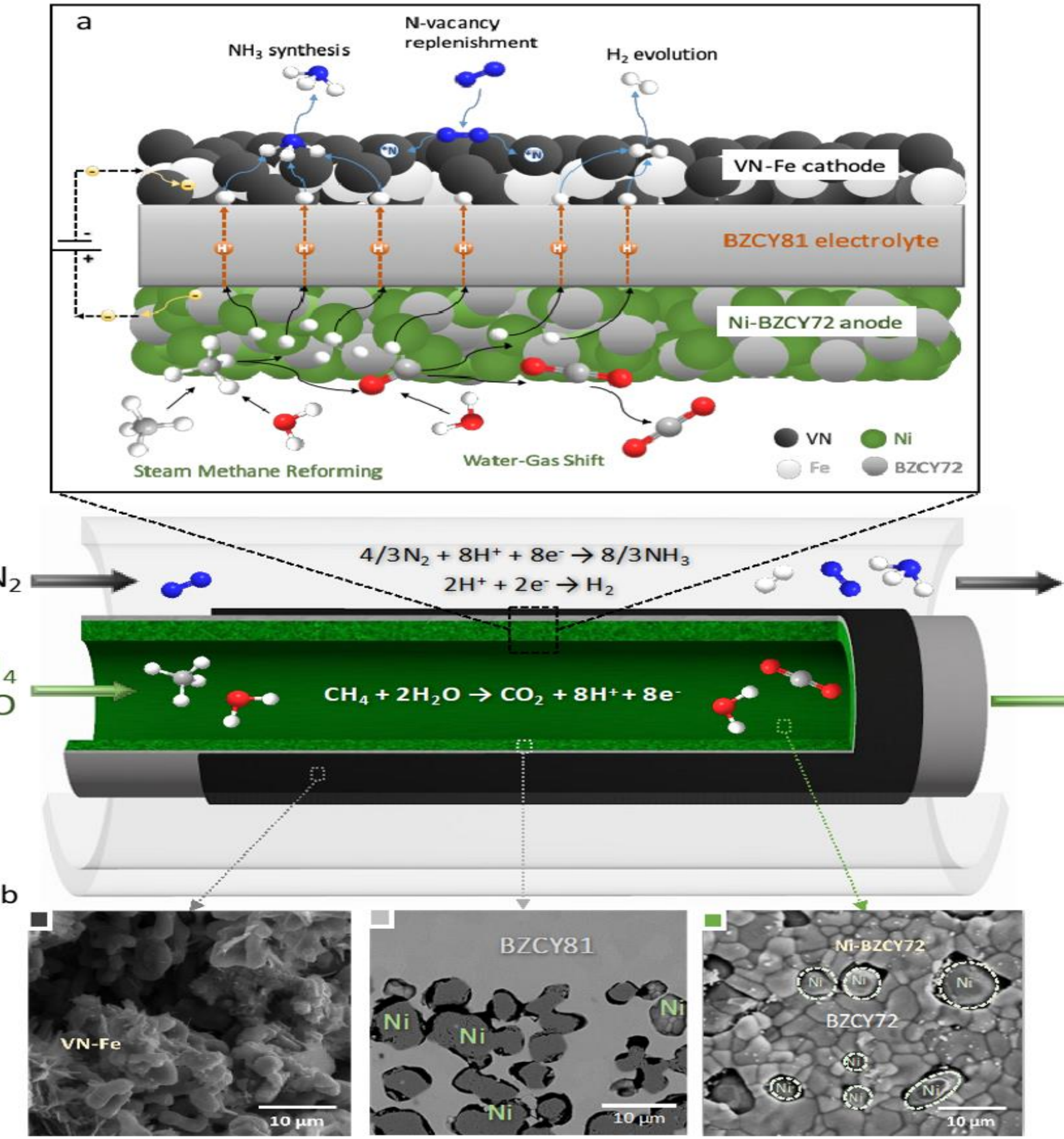
* * S. Robinson, et al, J. Membr. Sci. 446 (2013) 99–105; W.G. Coors, A. Manerbino, J. Membr. Sci. 376 (2011) 50–55.

Combined SSAS and CH_4-H_2O reforming



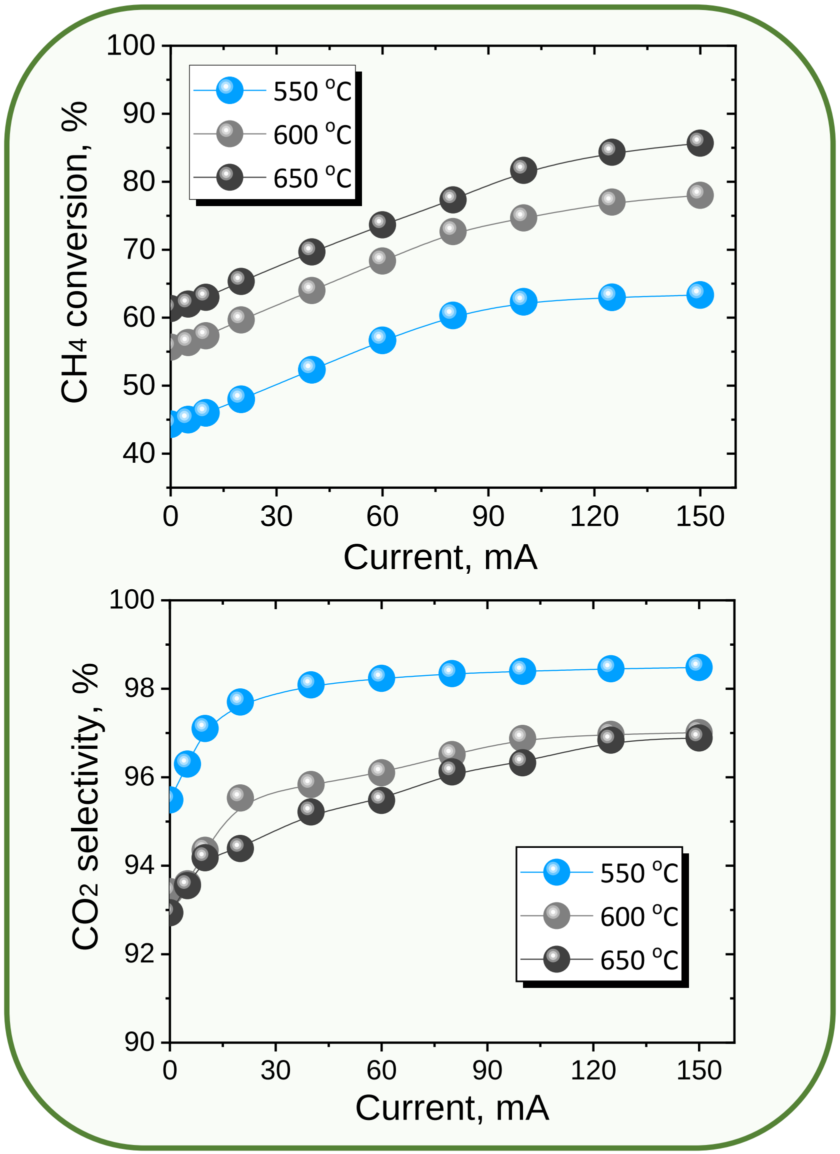
Overall: $3\ CH_4 + 6\ H_2O + 4\ N_2 \rightarrow 8\ NH_3 + 3\ CO_2$

- Methane conversion increases by H_2 removal (operation at lower T)
- Purification of hydrogen is eliminated

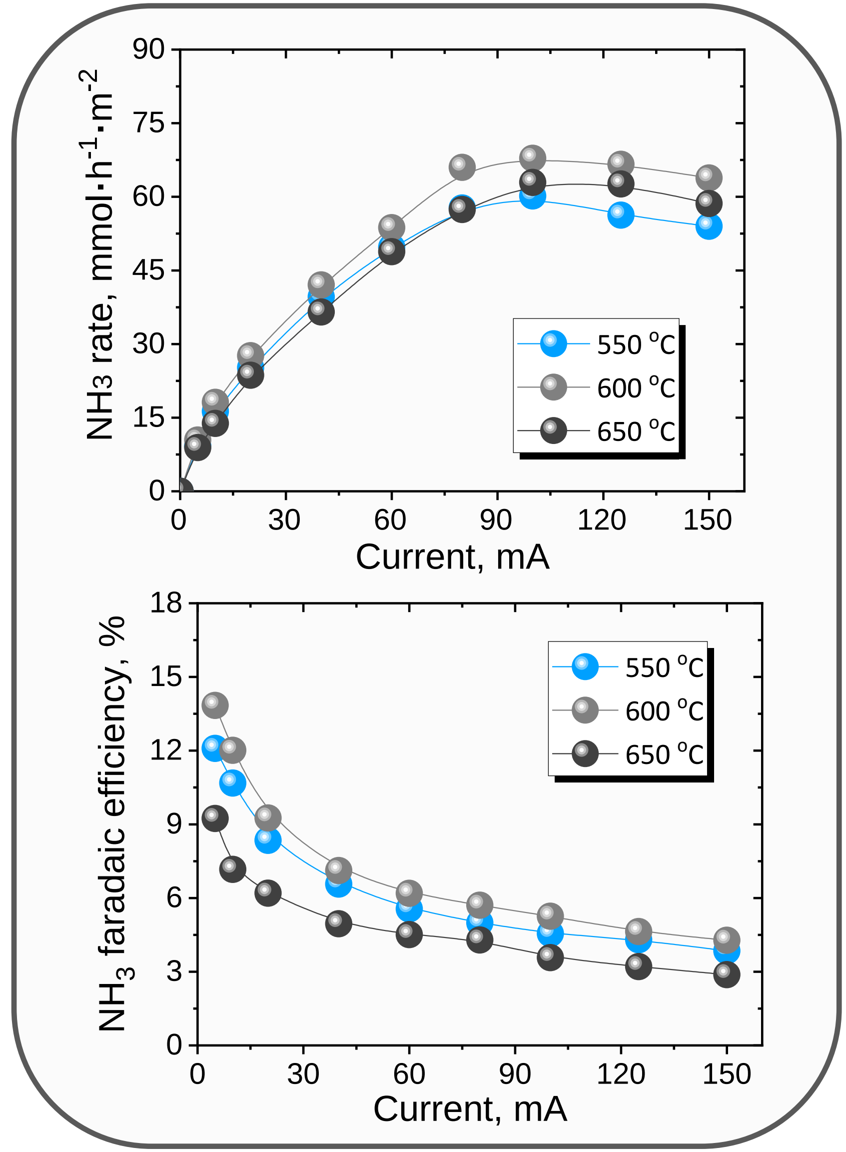

a
NH3 synthesis
N-vacancy replenishment
H2 evolution
VN-Fe cathode
BZCY81 electrolyte
Ni-BZCY72 anode
Steam Methane Reforming
Water-Gas Shift
VN
Ni
Fe
BZCY72
N2
4/3N2 + 8H+ + 8e- → 8/3NH3
2H+ + 2e- → H2
NH3
H2
N2
CH4
H2O
CH4 + 2H2O → CO2 + 8H+ + 8e-
CO2
H2O
b
VN-Fe
10 µm
BZCY81
Ni
10 µm
Ni-BZCY72
BZCY72
Ni
10 µm

Results of the combined process

Anode side



Cathode side



Summary of Experimental Results

At the anode:

- Open-circuit: methane conversion > 60%
- Closed-circuit: methane conversion up to 85%

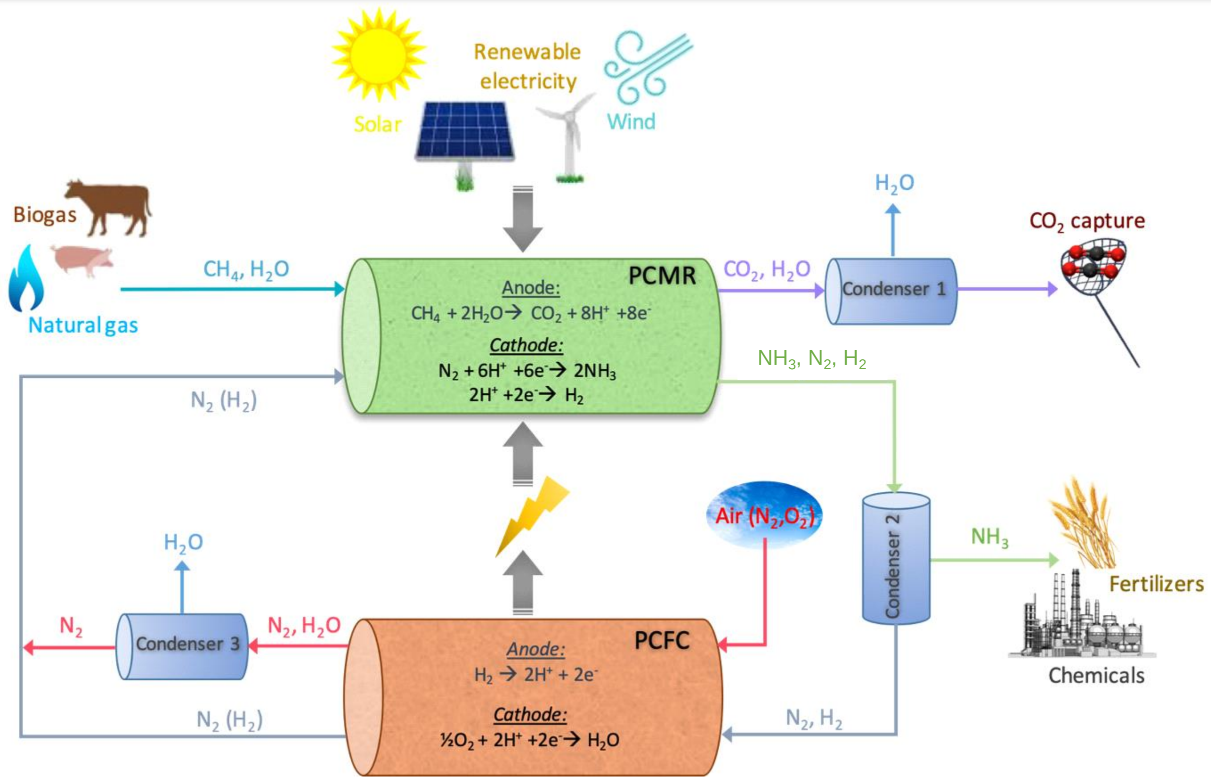
- Open-circuit: CO_2 selectivity up to 90%.
- Closed-circuit: CO_2 selectivity > 99%.

At the cathode:

- NH_3 is formed at a rate of up to 1.95 x 10^{-9} $mol{\cdot}s^{-1}{\cdot}cm^{-2}$ with a corresponding Faradaic Efficiency of 5.5%.

- FEs up to 14% at lower current densities

Visualizing an electrochemical HB



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

$N_2 + 6H^+ + 6e^- \leftrightarrow 2NH_3$ **(cathode)**

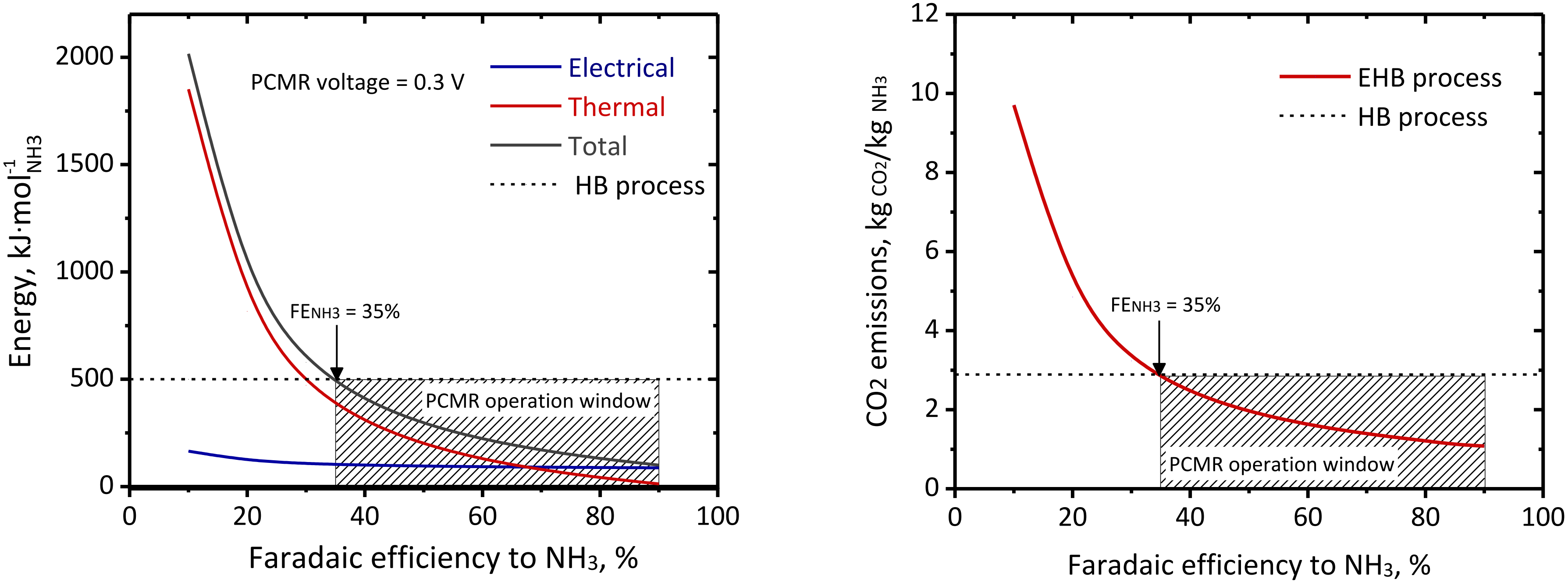
$2H^+ + 2e^- \leftrightarrow H_2$ **(cathode)**

Protonic Ceramic Fuel Cell: $H_2 \leftrightarrow 2H^+ + 2e^-$ **(anode)**

$1/2O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$ **(cathode)**

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

Electrochemical vs Industrial HB



- >35% FE is required to exhibit lower energy demands and CO_2 emissions than the industrial HB

What is the target

The "Giddey" Requirements[1]

- current density: **0.25-0.5 A cm^{-2}**
- current efficiency : **>50%**
- NH_3 is production rates: **4.3 - 8.7 x 10^{-7} mol cm^{-2} s^{-1}**

The DOE (REFUEL) Requirements[2]

- current density: **0.3 A cm^{-2}**
- Faradaic efficiency : **90%**
- NH_3 is production rates: **9.3 x10^{-7} mol cm^{-2} s^{-1}**

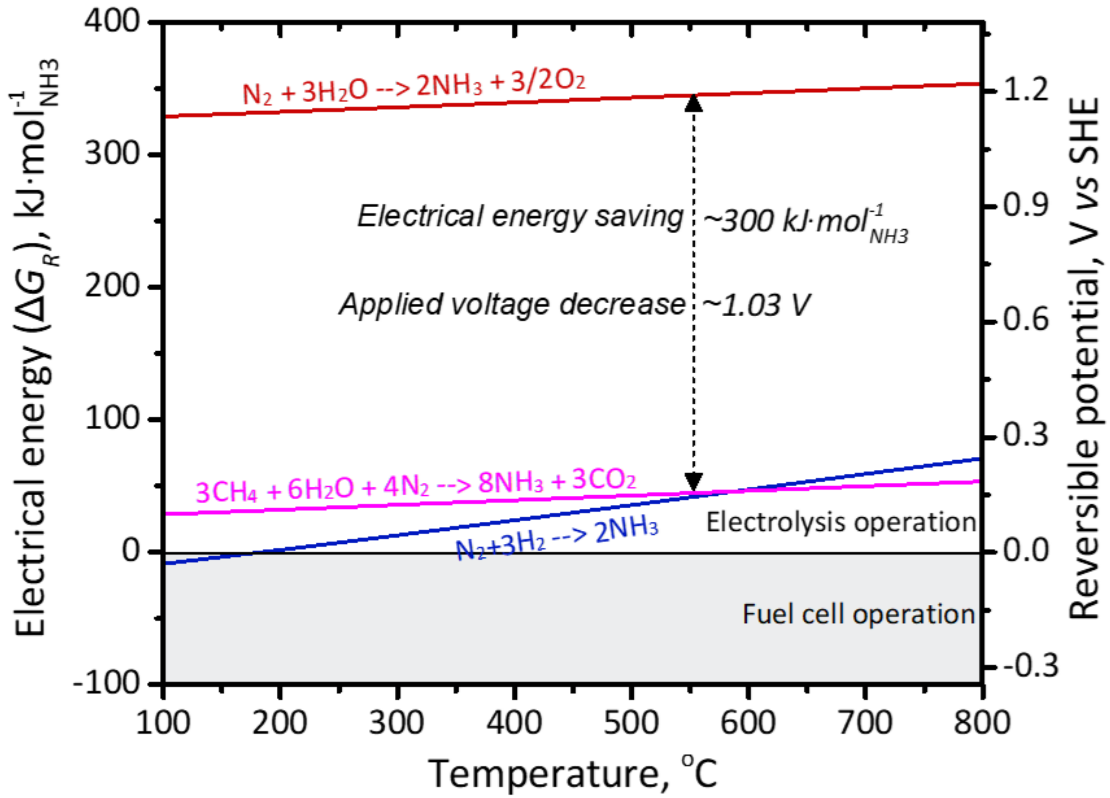
1 S..Giddey et al, Int'l J. Hydrogen Energy 38, pp. 14576-14594 (2013)
2 I.McPherson, J. Zhang, JOULE, 4, pp. 12-14 (2020)]

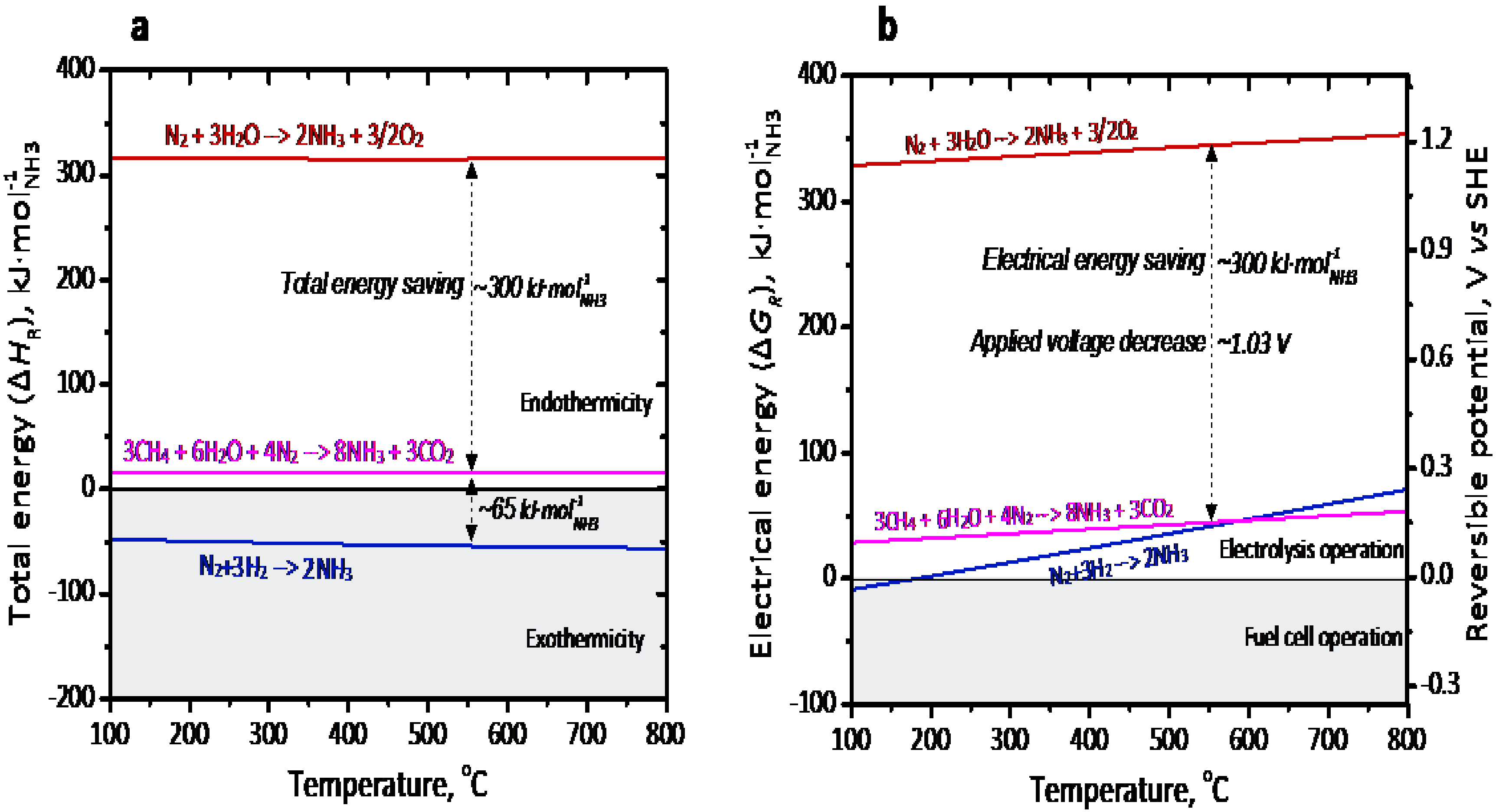
Increasing the Faradaic Efficiency to a 40-50% and the NH_3 production rate to 5×10^{-7} mol cm^{-2} s^{-1} is a real challenge. It will require intense collaboration among researchers in the fields of electrochemistry, heterogeneous catalysis and materials science.

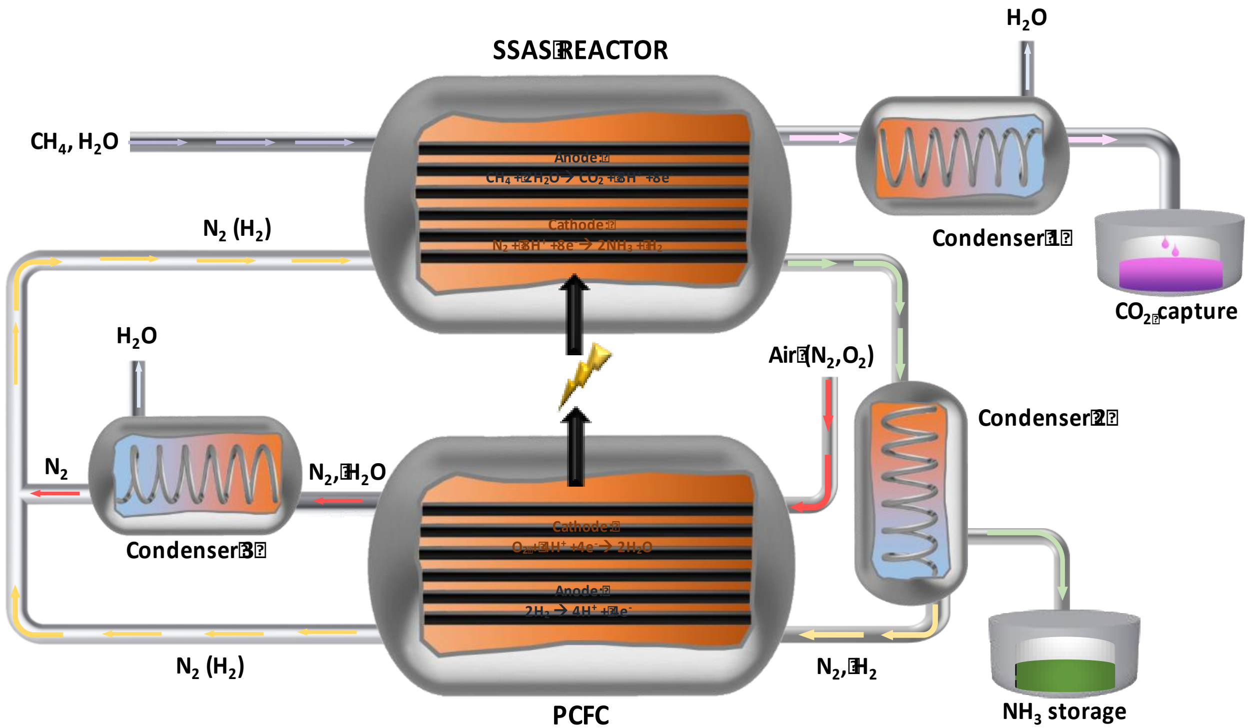
But it is worth the effort…

Thank you for your attention!

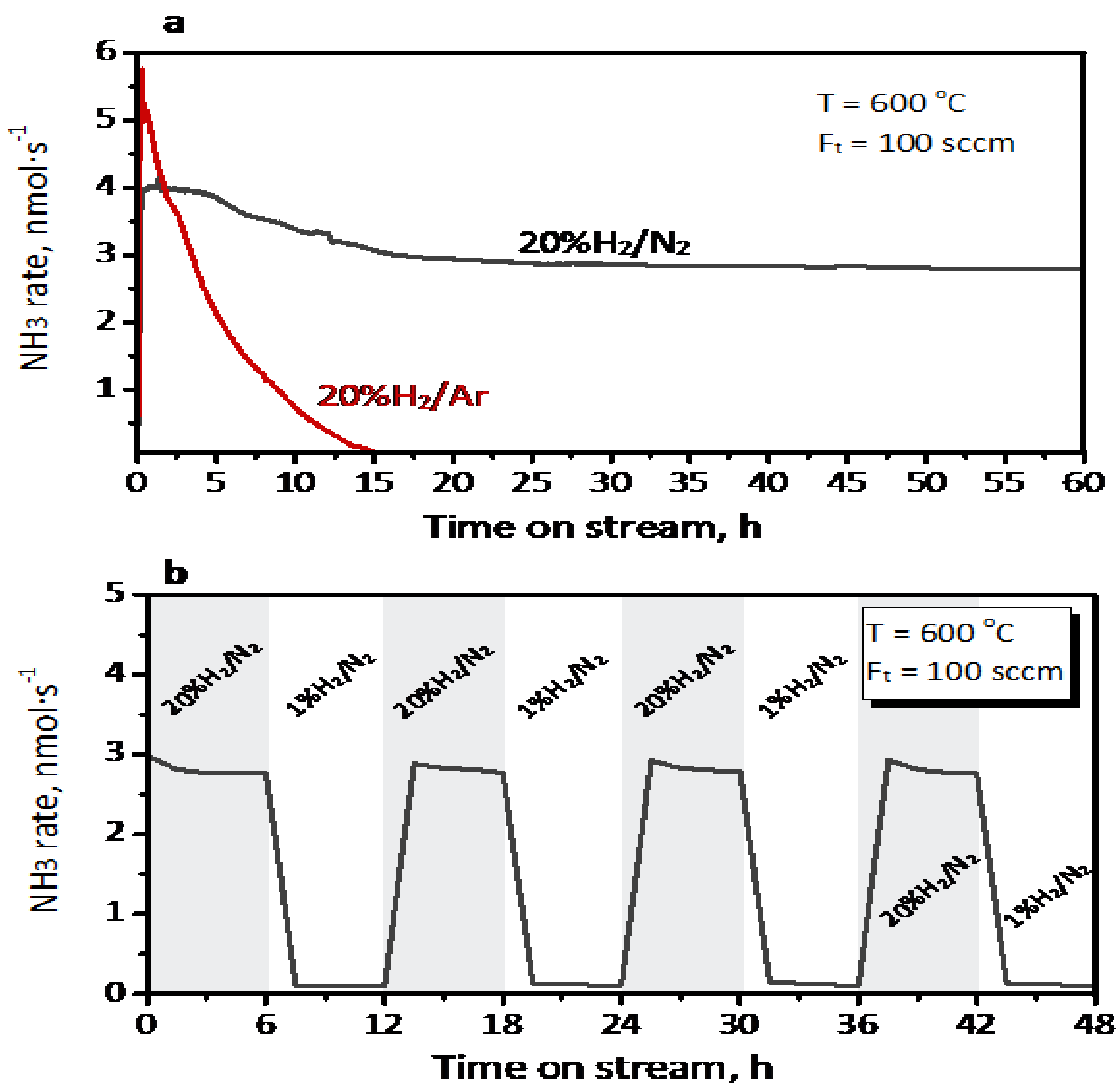
Electrical energy demands

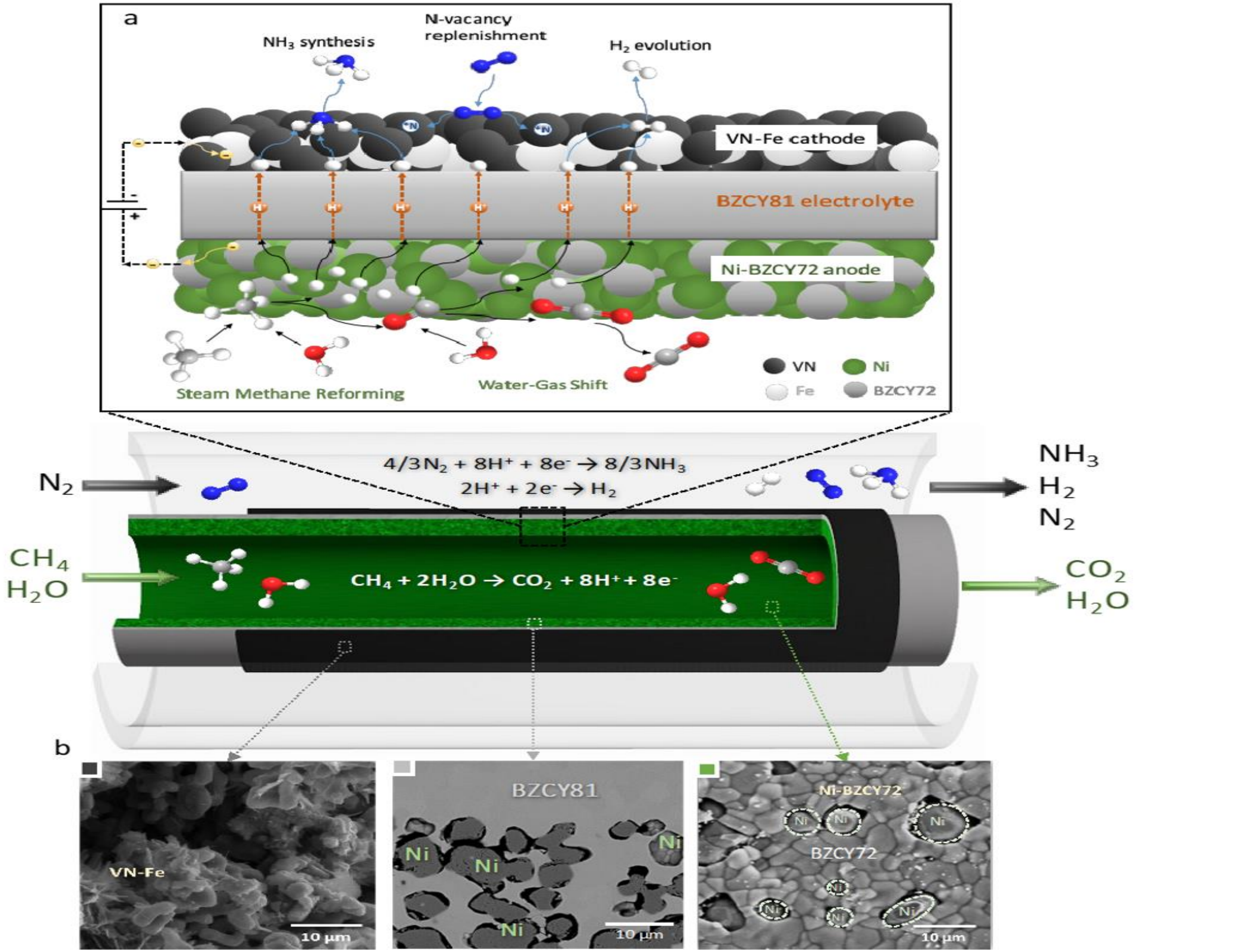



a
Total energy (ΔH_R), kJ·mol⁻¹ NH3
N2 + 3H2O --> 2NH3 + 3/2O2
Total energy saving
~300 kJ·mol⁻¹ NH3
Endothermicity
3CH4 + 6H2O + 4N2 --> 8NH3 + 3CO2
~65 kJ·mol⁻¹ NH3
N2+3H2 --> 2NH3
Exothermicity
Temperature, °C
b
Electrical energy (ΔG_R), kJ·mol⁻¹ NH3
Reversible potential, V vs SHE
N2 + 3H2O --> 2NH3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



SSAS REACTOR
CH4, H2O
Anode:
CH4 + 2H2O → CO2 + 8H+ +8e-
Cathode:
N2 + 8H+ +8e- → 2NH3 + H2
H2O
Condenser 1
CO2 capture
N2 (H2)
Air (N2,O2)
Condenser 2
H2O
N2
N2, H2O
Condenser 3
Cathode:
O2 + 4H+ +4e- → 2H2O
Anode:
2H2 → 4H+ + 4e-
N2 (H2)
N2, H2
NH3 storage
PCFC


a
T = 600 °C
Ft = 100 sccm
20%H2/N2
20%H2/Ar
NH3 rate, nmol·s-1
Time on stream, h
b
T = 600 °C
Ft = 100 sccm
20%H2/N2
1%H2/N2
NH3 rate, nmol·s-1
Time on stream, h



a
NH3 synthesis
N-vacancy replenishment
H2 evolution
VN-Fe cathode
BZCY81 electrolyte
Ni-BZCY72 anode
Steam Methane Reforming
Water-Gas Shift
VN
Ni
Fe
BZCY72
4/3N2 + 8H+ + 8e- → 8/3NH3
2H+ + 2e- → H2
N2
NH3
H2
N2
CH4
H2O
CH4 + 2H2O → CO2 + 8H+ + 8e-
CO2
H2O
b
VN-Fe
10 µm
BZCY81
Ni
Ni
Ni
Ni
10 µm
Ni-BZCY72
BZCY72
Ni
10 µm