Electrocatalytic Synthesis of Ammonia at Room Temperature and Atmospheric Pressure from Water and Nitrogen on a Carbon-Nanotube-Based Electrocatalyst

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Joseph Salamoun
Current Literature 02/11/17
Wipf Group

Production of Ammonia

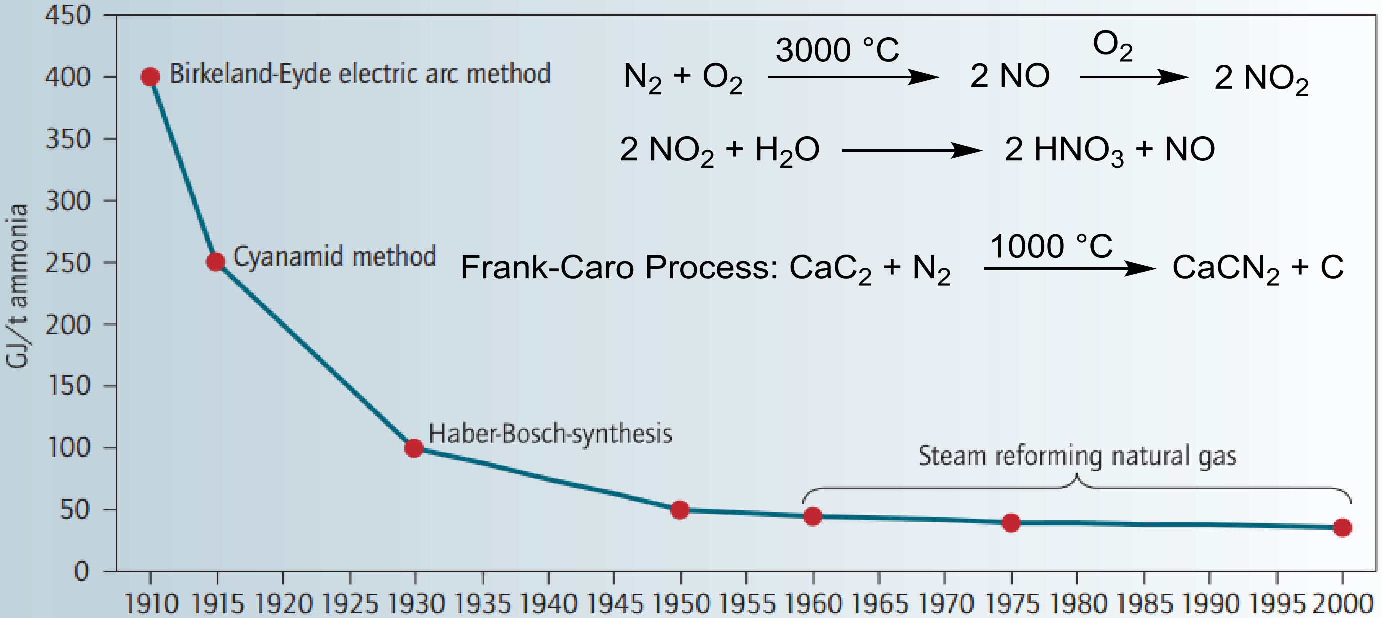
- Annual production > 150 million tons. Nearly 80% of ammonia used in fertilizers.
- Resulted in 3 Nobel Prizes in Chemistry (Haber 1918, Bosch 1931, Ertl 2007)
- Most common production process is the Haber-Bosch process.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

- Contributes to nearly 1.4% of global energy consumption and 3% of global CO_2 emissions.

Advancements in Ammonia Synthesis

Figure 5: Ammonia synthesis breakthrough and energy efficiency



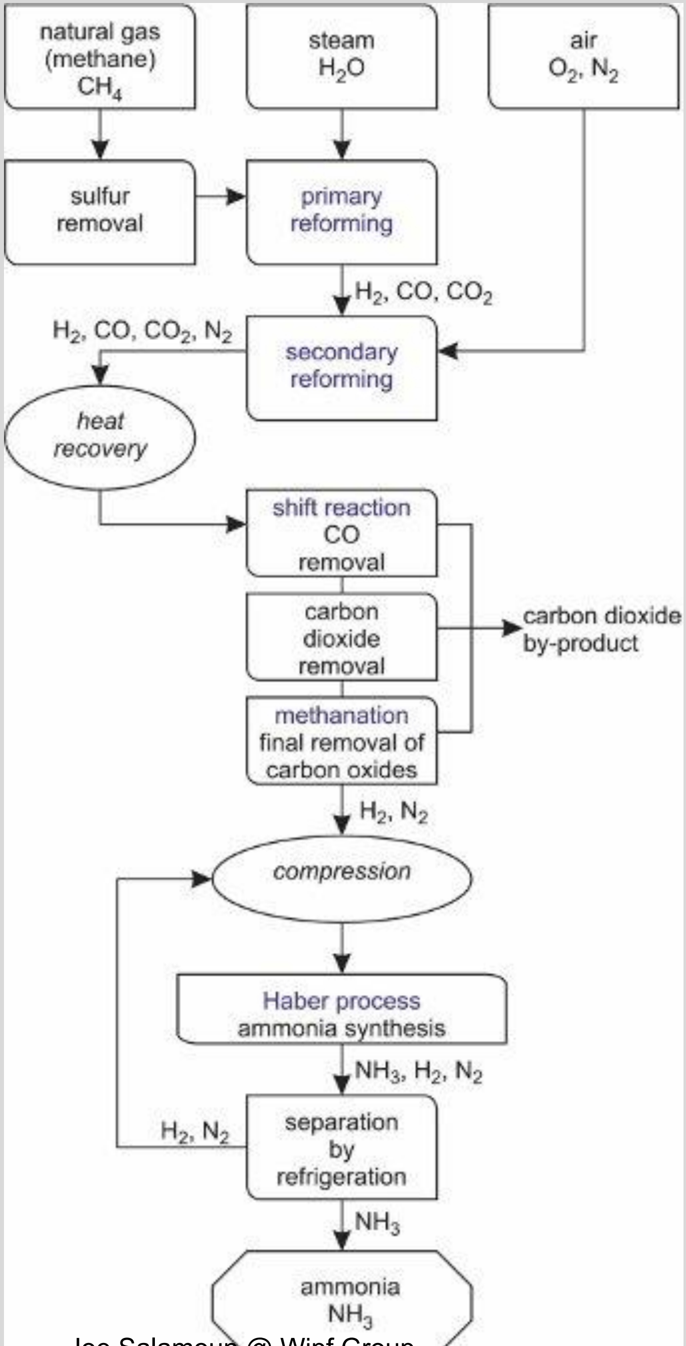
Source: reproduced from P. Broadhurst, *Catalysts to Drive Environmental Improvements in Fertilizer Manufacture*, Johnson Mathey Catalysts: www.faidelhi.org/FAI%20Seminar%202008/Presentations/Session%20III/Presentation%205.pdf.

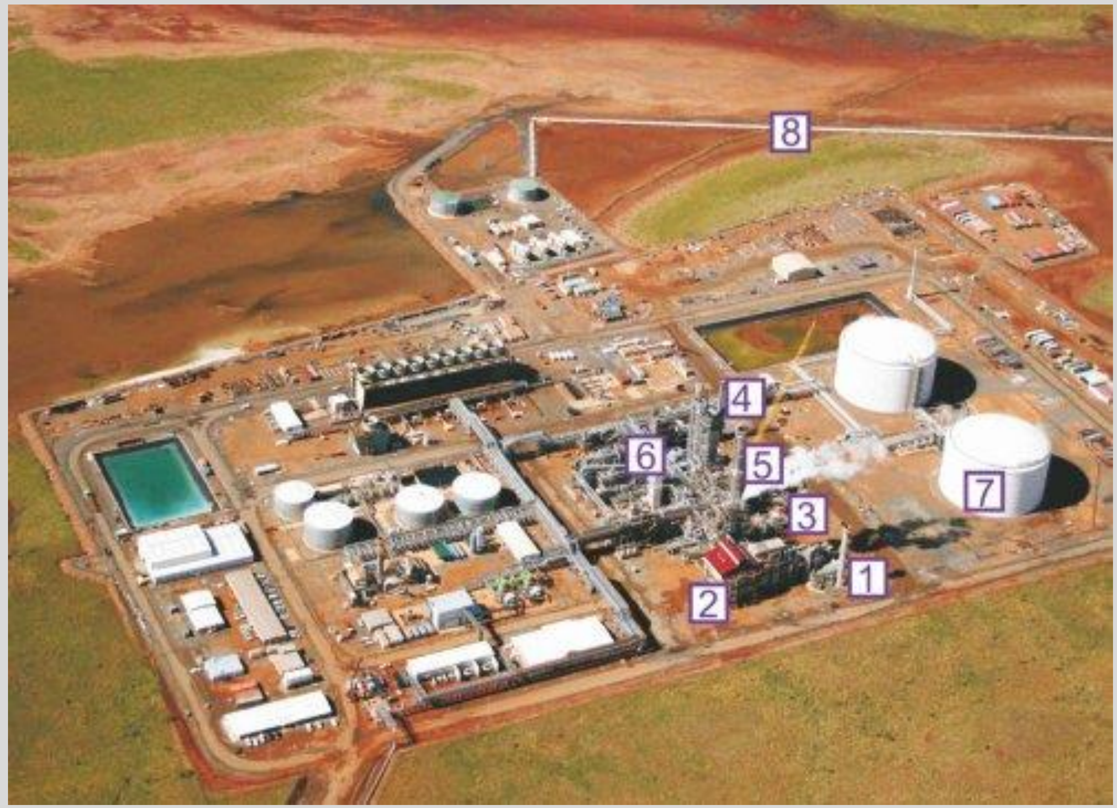
KEY POINT: Dramatic improvements in energy use for ammonia occurred prior to 1930, over the last five decades improvements have been more incremental.

Average annual American household energy consumption in 2015 is ca. 39 GJ.

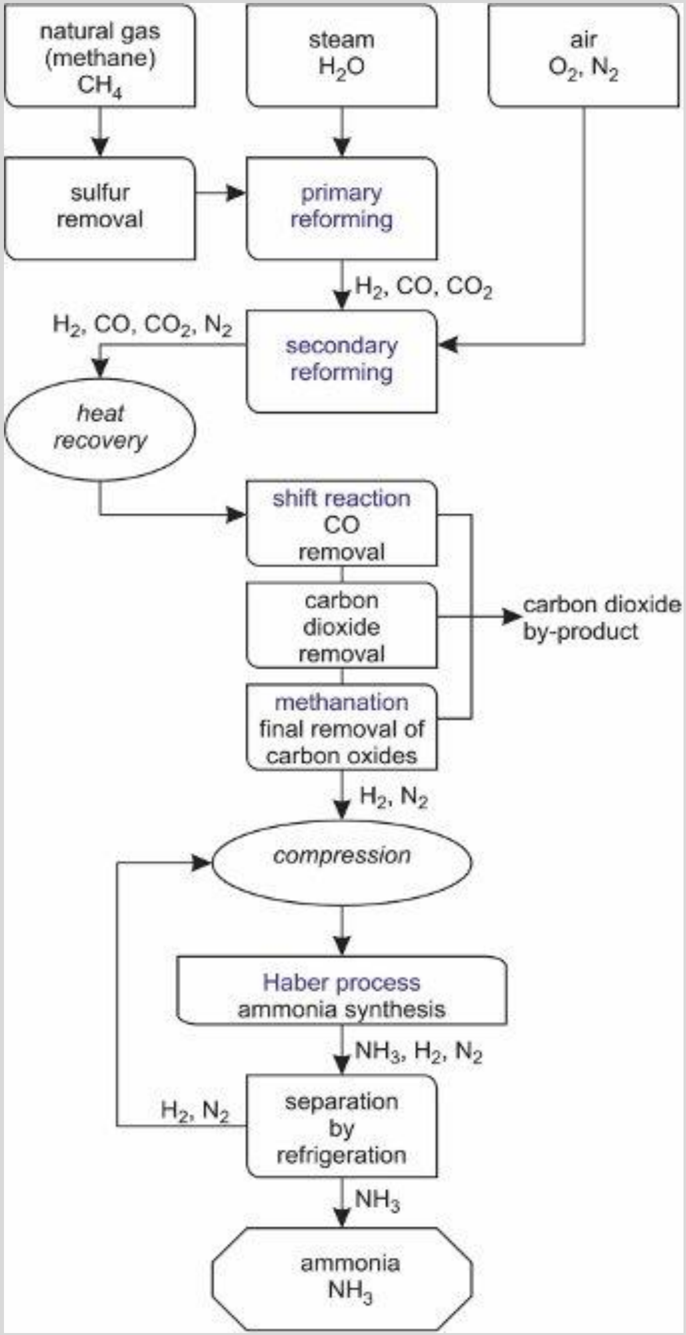
https://www.iea.org/publications/freepublications/publication/Chemical_Roadmap_2013_Final_WEB.pdf

Industrial Synthesis of Ammonia





http://www.essentialchemicalindustry.org/chemicals/ammonia.html



Methane (Natural Gas) is the Source of Hydrogen Gas

- Sulfides in methane must be removed.

$$\text{R-SH (g)} + H_2\text{ (g)} \xrightarrow[\text{ca. 700 K}]{\text{mixed oxides of Co and Mo supported on alumina}} \text{R-H (g)} + H_2S\text{ (g)}$$

$$\text{ZnO (s)} + H_2S\text{ (g)} \xrightarrow[\text{ca. 700 K}]{} \text{ZnS (s)} + H_2O\text{ (g)}$$

Primary steam reforming:

$$CH_4\text{ (g)} + H_2O\text{ (g)} \underset{\text{ca. 1000 K, 30 atm, tubular reactor}}{\overset{\text{Ni catalyst supported on } CaO/Al_2O_3}{\rightleftharpoons}} \text{CO (g)} + 3\ H_2\text{ (g)}$$

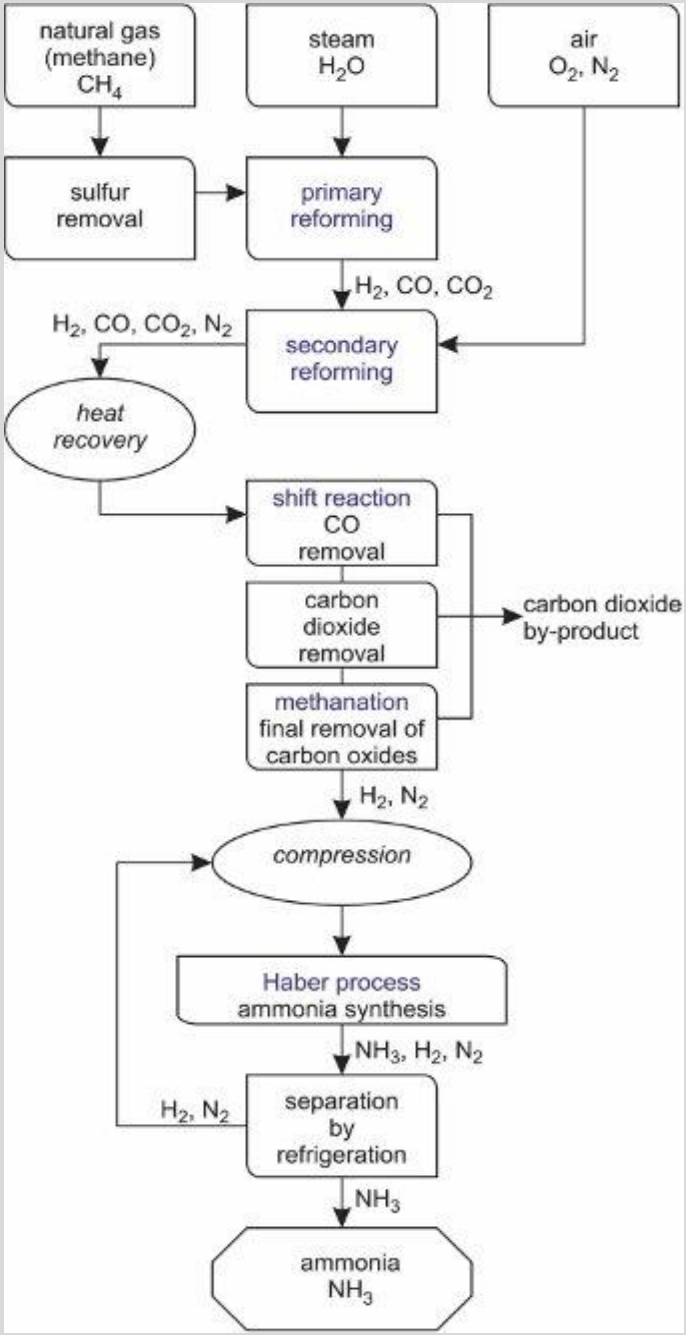
Secondary steam reforming:

$$2\ H_2\text{ (g)} + O_2\text{ (g)} \longrightarrow 2\ H_2O\text{ (g)}$$

$$CH_4\text{ (g)} + H_2O\text{ (g)} \underset{\text{ca. 1200 K}}{\overset{\text{Ni catalyst}}{\rightleftharpoons}} \text{CO (g)} + 3\ H_2\text{ (g)}$$

- Shift Rxn converts CO to CO_2.
- Methanation reduces trace CO and CO_2 to CH_4.
- Result: 74% H_2, 25% N_2, 1% methane, trace Ar.

http://www.essentialchemicalindustry.org/chemicals/ammonia.html



Ammonia Production

The Haber Process:

$$N_2\,(g) + 3H_2\,(g) \underset{\text{fixed bed reactor}}{\overset{\text{Fe catalyst}}{\rightleftharpoons}} 2\,NH_3\,(g)$$

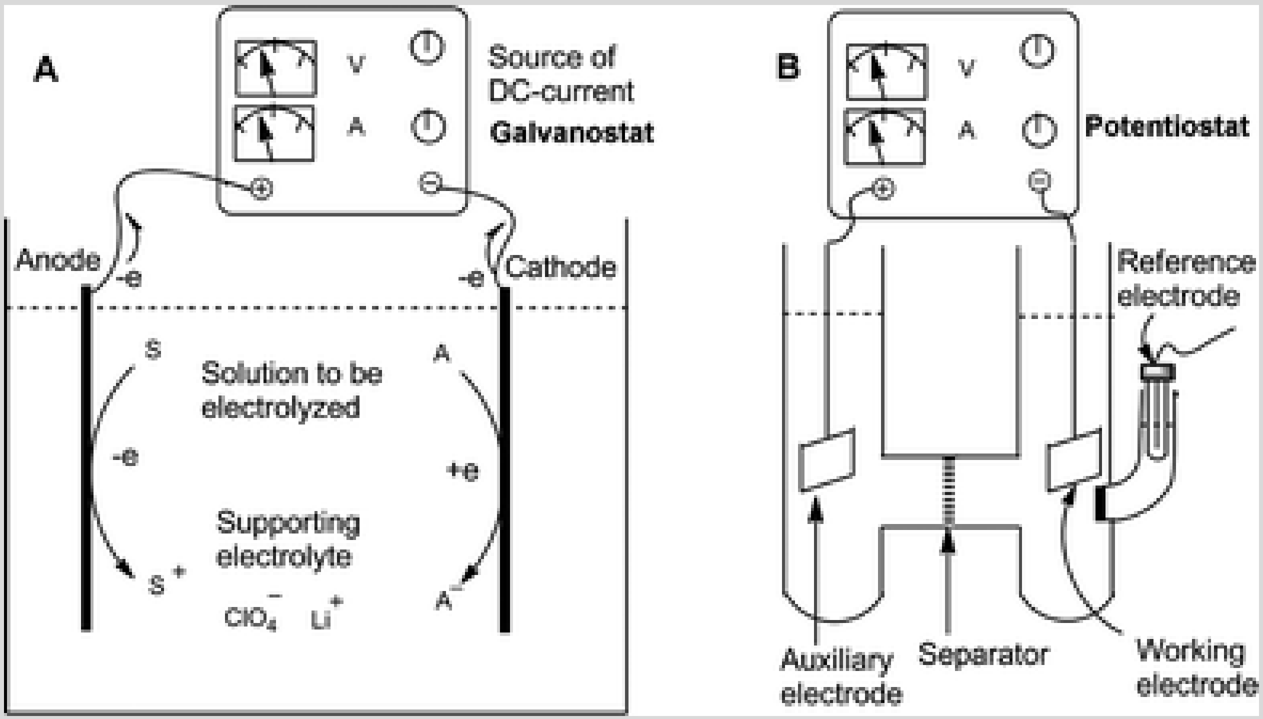
ΔH = - 92 kJ/mol

% ammonia present at equilibrium

Pressure (atm)	373 K	473 K	573 K	673 K	773 K
10	-	50.7	14.7	3.9	1.2
25	91.7	63.6	27.4	8.7	2.9
50	94.5	74.0	39.5	15.3	5.6
100	96.7	81.7	52.5	25.2	10.6
200	98.4	89.0	66.7	38.8	18.3
400	99.4	94.6	79.7	55.4	31.9
1000	-	98.3	92.6	79.8	57.5

http://www.essentialchemicalindustry.org/chemicals/ammonia.html

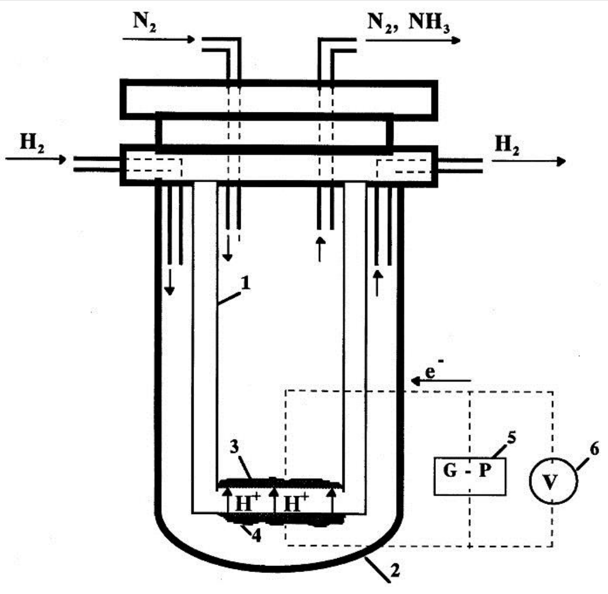
Components of Electrochemical Cell



- A **galvanostat** (also known as amperostat) controls the current (measured in Amps). Current is the rate at which charge is flowing.
- A **potentiostat** controls the voltage difference between a Working Electrode and a Reference Electrode. Both electrodes are contained in an electrochemical cell.

Green Chem. **2010**, *12*, 2099.

Research into Electroproduction of Ammonia

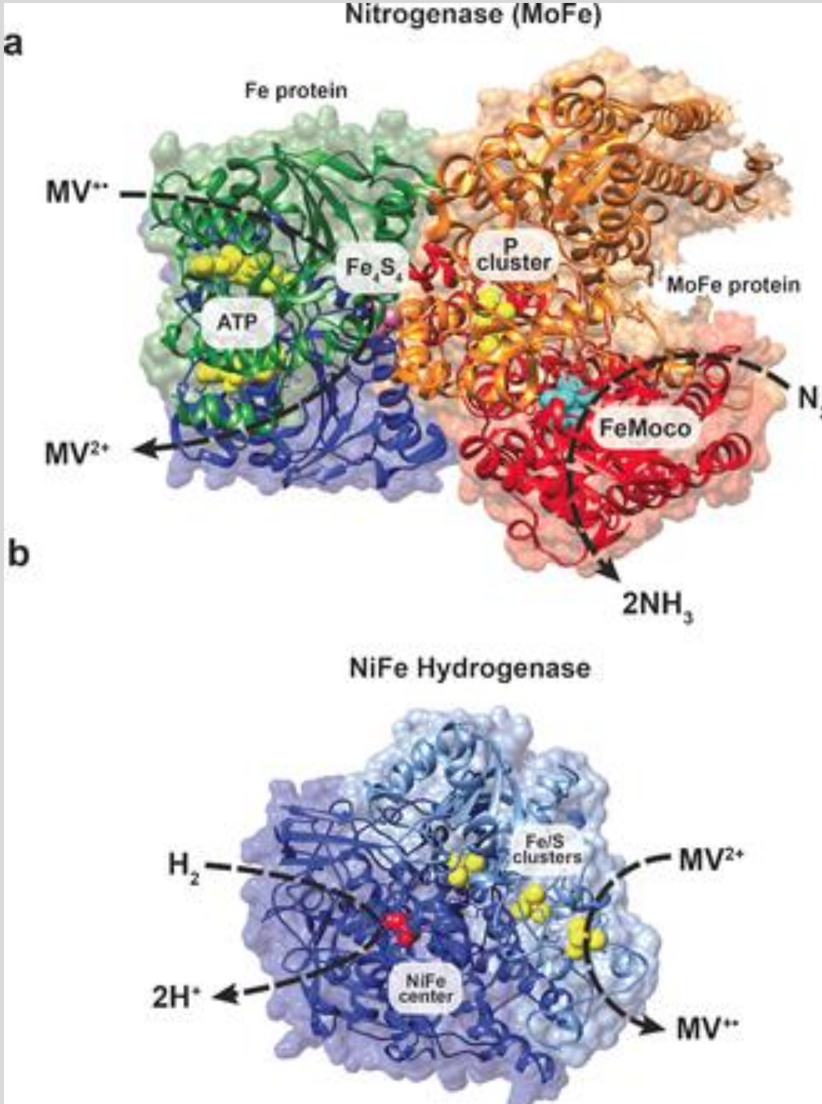


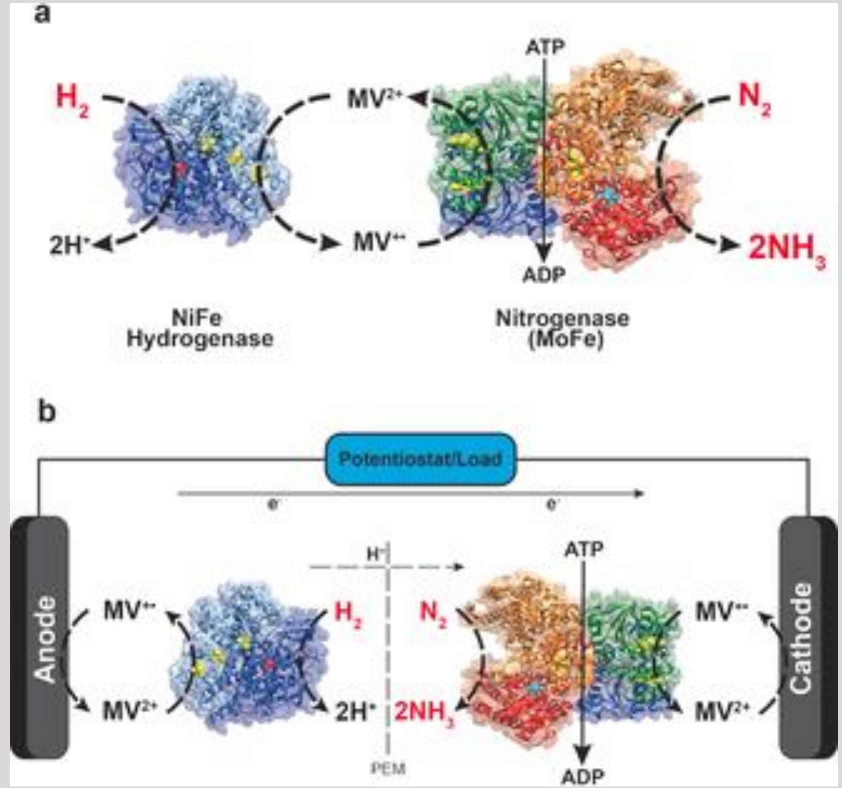
- Ammonia was synthesized from H_2 (g) and N_2 (g) using a solid state proton (H^+)-conducting cell-reactor with Pd electrodes at 570 °C and atmospheric pressure. >78% of electrochemically supplied hydrogen was converted into ammonia.
  - *Science* **1998**, *282*, 98.

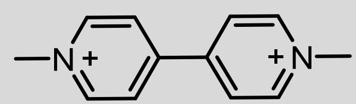
- Electrolysis of air and steam in a molten hydroxide (0.5 NaOH/0.5 KOH) suspension on nano-Fe_2O_3 at 200 °C produced ammonia at coulombic efficiency of 35%.
  - *Science* **2014**, *345*, 637.

- Electrolysis of H_2O and N_2 at Ru cathodes, using a solid polymer electrolyte cell. At atmospheric pressure and 90 °C with a current efficiency of 0.2%, ammonia was produced at a rate of 1.2 μg h^{-1} cm^{-2}.
  - *Chem. Commun.* **2000**, 1673.

Bioelectrochemical Synthesis of Ammonia







Methyl Viologen (MV)

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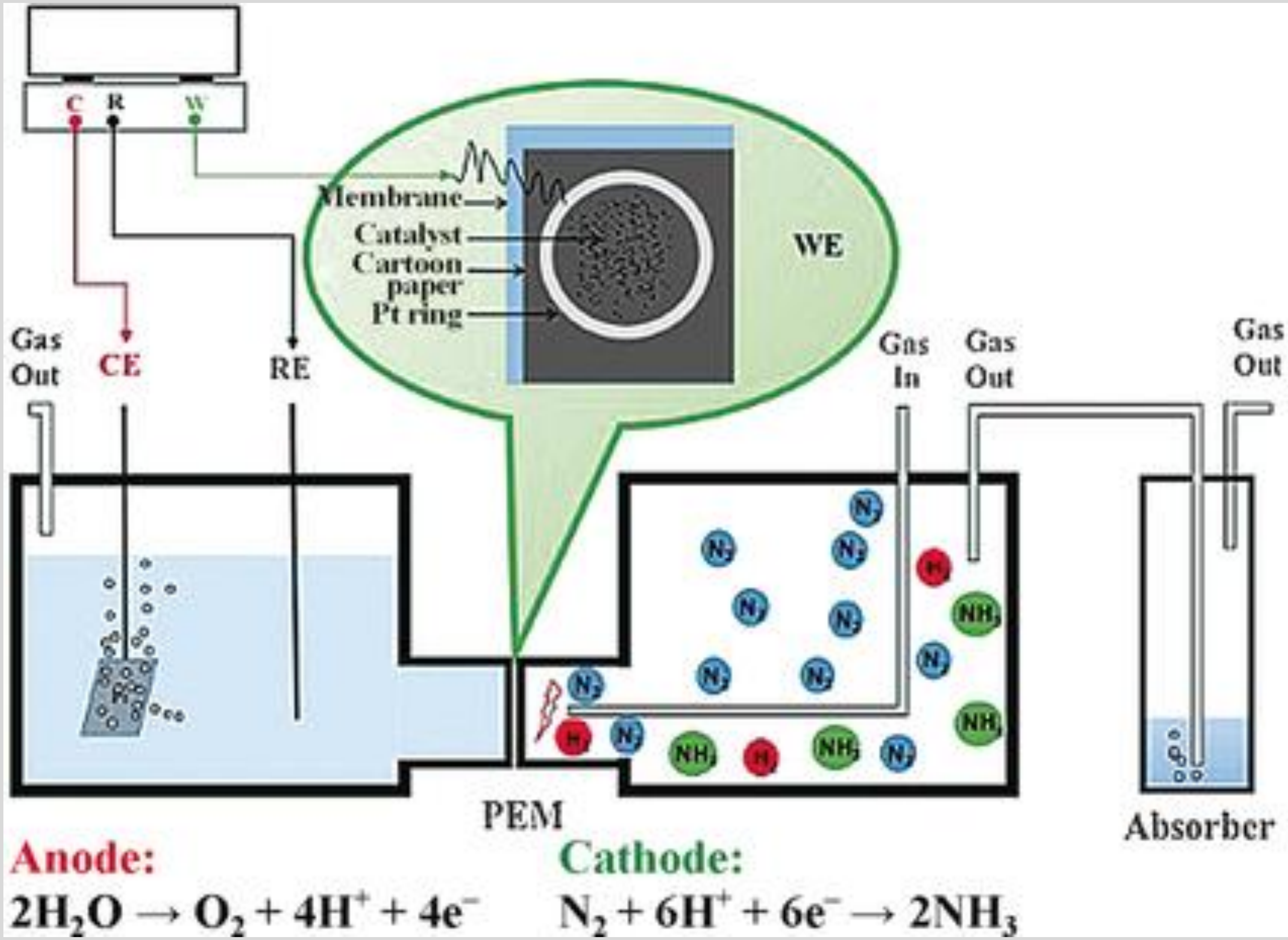
The Assembly



- Anode chamber contains a dilute solution of $KHCO_3$.
- The membrane-electrode assembly is the cathode/WE. Made with Nafion membrane (sulfonated tetrafluoroethylene), gas diffusion layer, and Fe_2O_3 support on conductive carbon nanotube.

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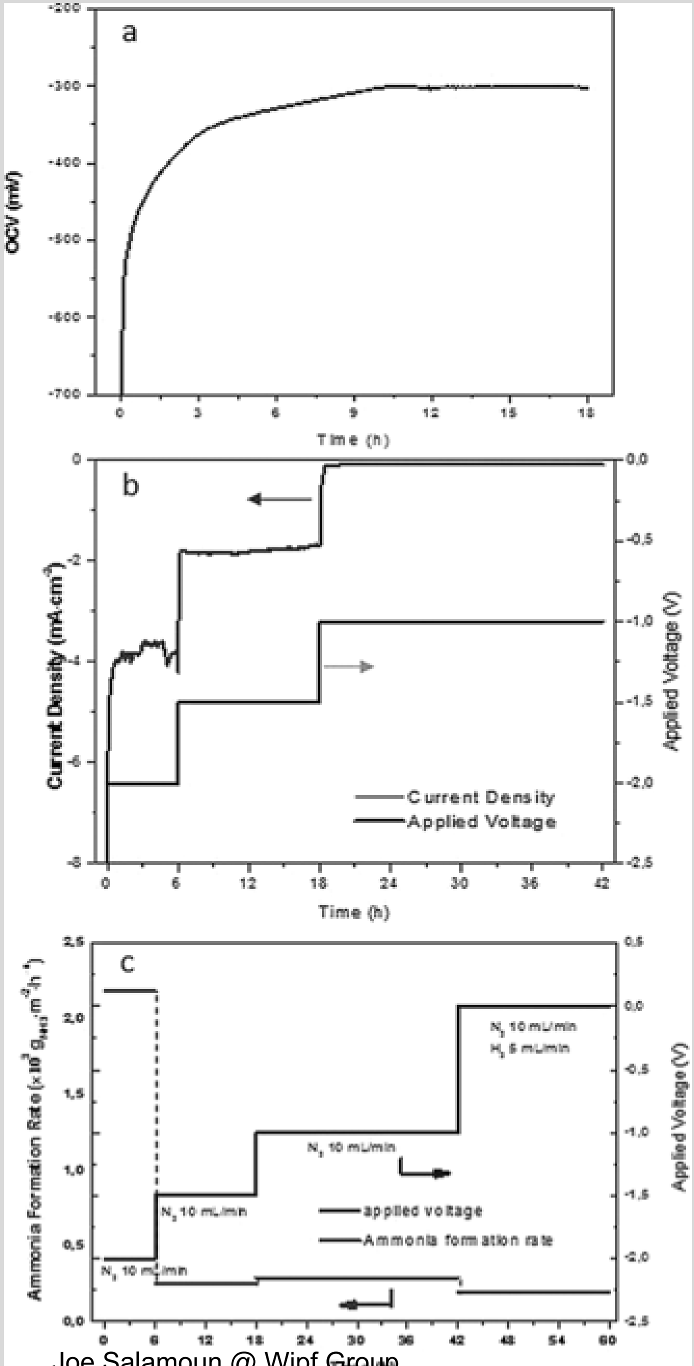

Reaction Parameters

- OCV (open circuit potential) = without application of potential.
    - Introduced N_2 and H_2 (2:1)
    - Used to monitor base reaction(s)
    - Shows partial reduction of Fe_2O_3
- Potential is related to free energy change of a reaction. $E° = - G_R°/nF$

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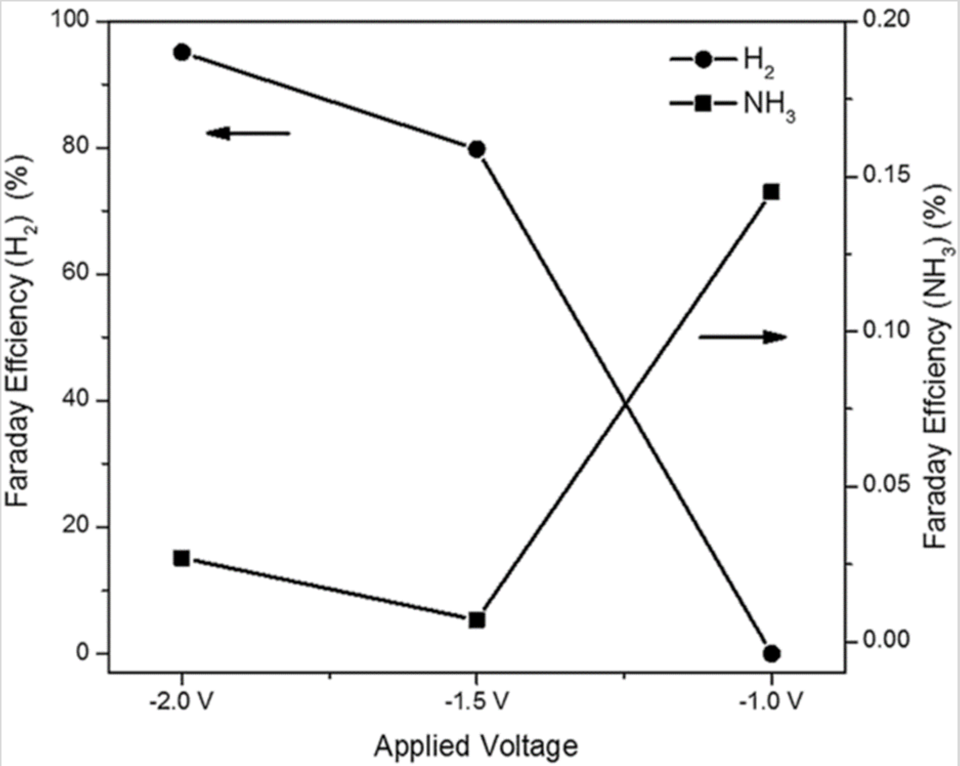
Reaction Efficiency

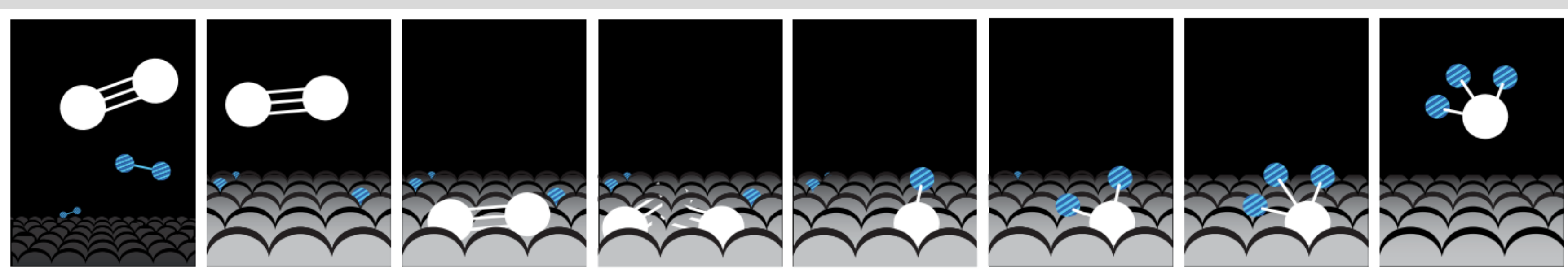


Faraday efficiency describes the efficiency with which electrons are transferred in a system facilitating an electrochemical reaction.

Low efficiency may indicate poor conversion or side reactions.

$$FE_{NH_3}(\%) = \frac{3 \times R_{NH_3}(mol \cdot cm^{-2} \cdot s^{-1}) \times t(s) \times S(cm^{-2}) \times F}{I(A) \times t(s)} \times 100\%$$

$$FE_{H_2}(\%) = \frac{2 \times P_{H_2}(\%) \times F_{N_2}(mL/min) \times t(s) \div 60(s/min) \times F}{I(A) \times t(s) \times V_m(L/mol) \times 10^3(mL/L)} \times 100\%$$



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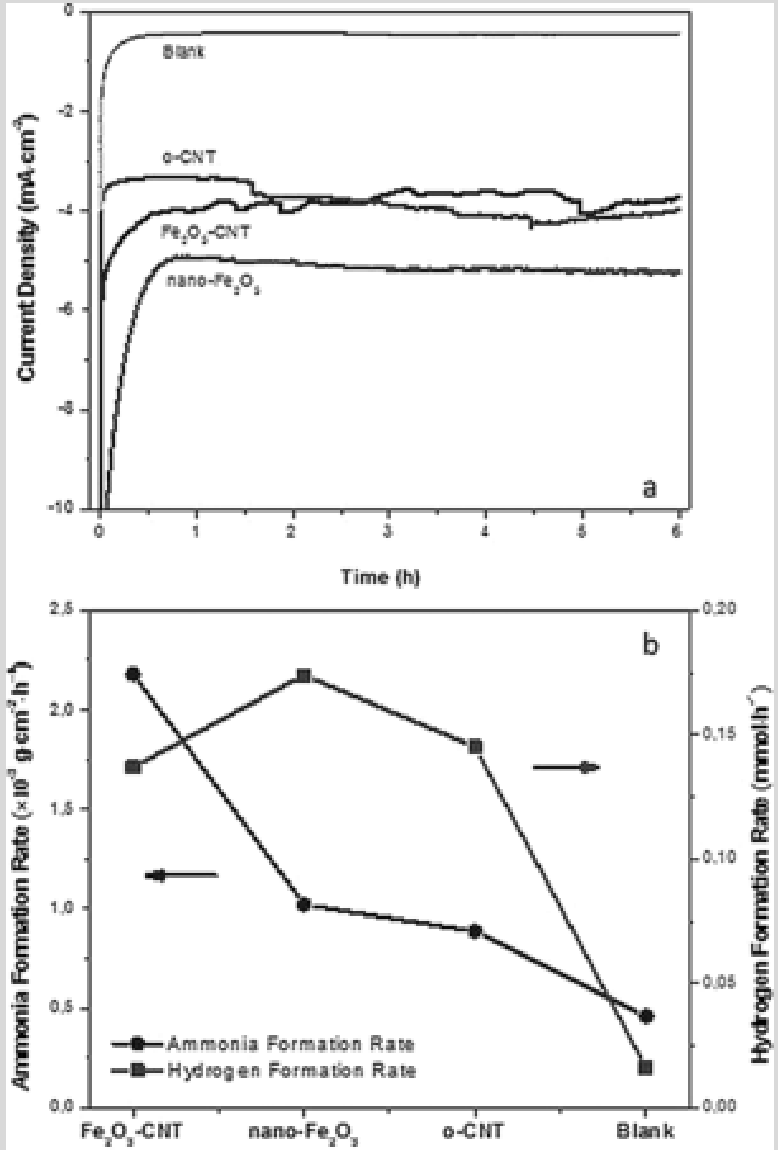
https://www.nobelprize.org/nobel_prizes/chemistry/laureates/2007/popular-chemistryprize2007.pdf

Catalyst Surface Makes a Difference



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Conclusions

- An important proof-of-concept of ammonia formation at room temperature and atmospheric pressure.
- Uses abundant reactants (water and nitrogen gas) and catalyst (iron and carbon nanotubes).
- Electricity introduces the possibility of renewable and green energy sources.
- Reaction rate, scale, and efficiency remain a challenge.