Integrated Electrochemical–Thermal Ammonia Production Process

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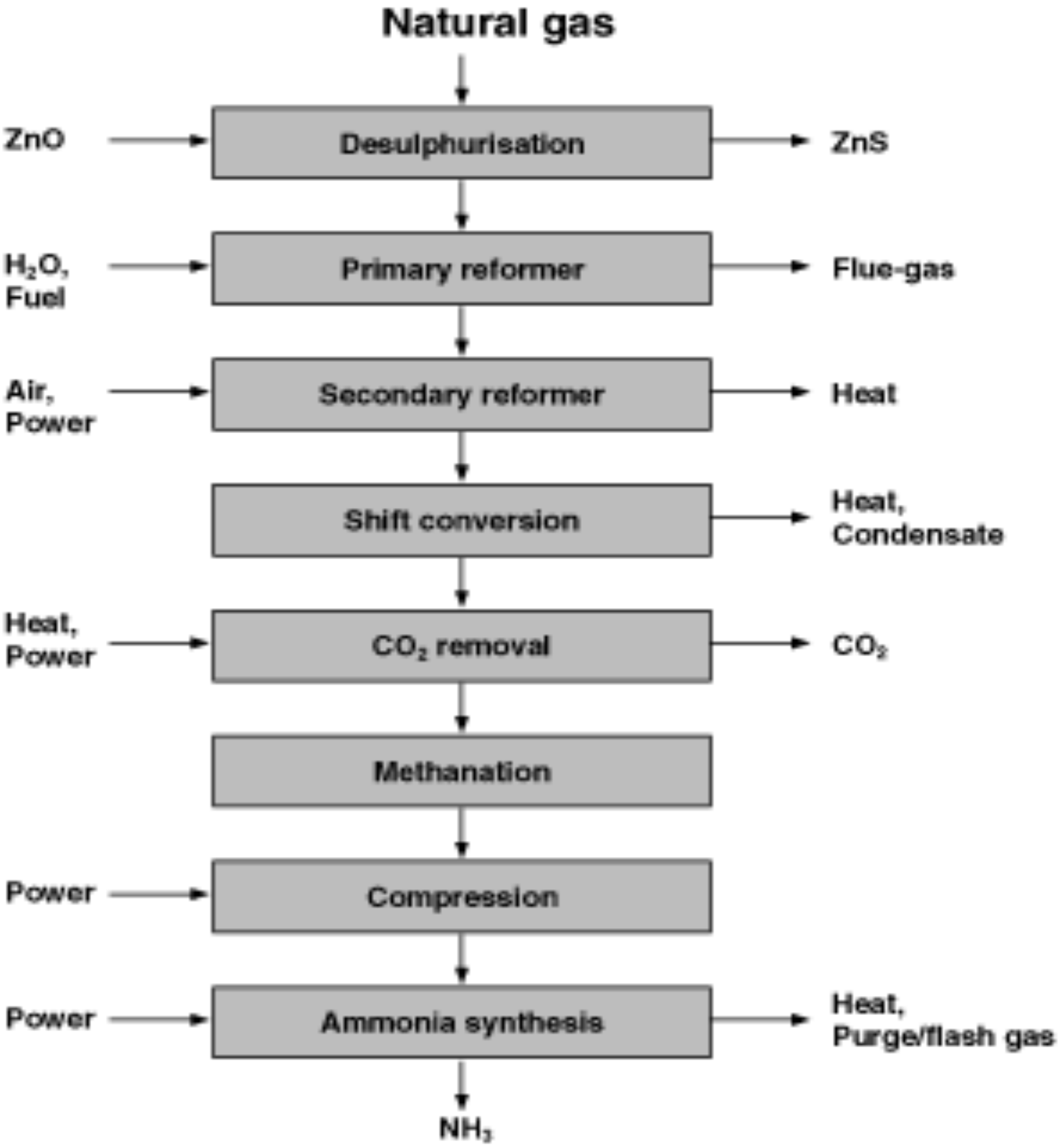
Haber–Bosch ammonia process



- **Reaction:**

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

$\Delta H = -92$ kJ mol^{-1}

- **Reaction conditions:**

Temperature: 430–480°C

Pressure: 150–300 atm

Catalyst: Iron-based

Yield: ~15%

Haber limitations for renewable ammonia production

- Achieving economic viability requires production capacity of ~1000 tons/day, which is typically beyond range of economic renewable feedstock supply
- High capital cost due to high pressure operational requirements (compressor, piping, containment vessels, etc.) hinders small-scale operation
- Requires expensive high purity hydrogen

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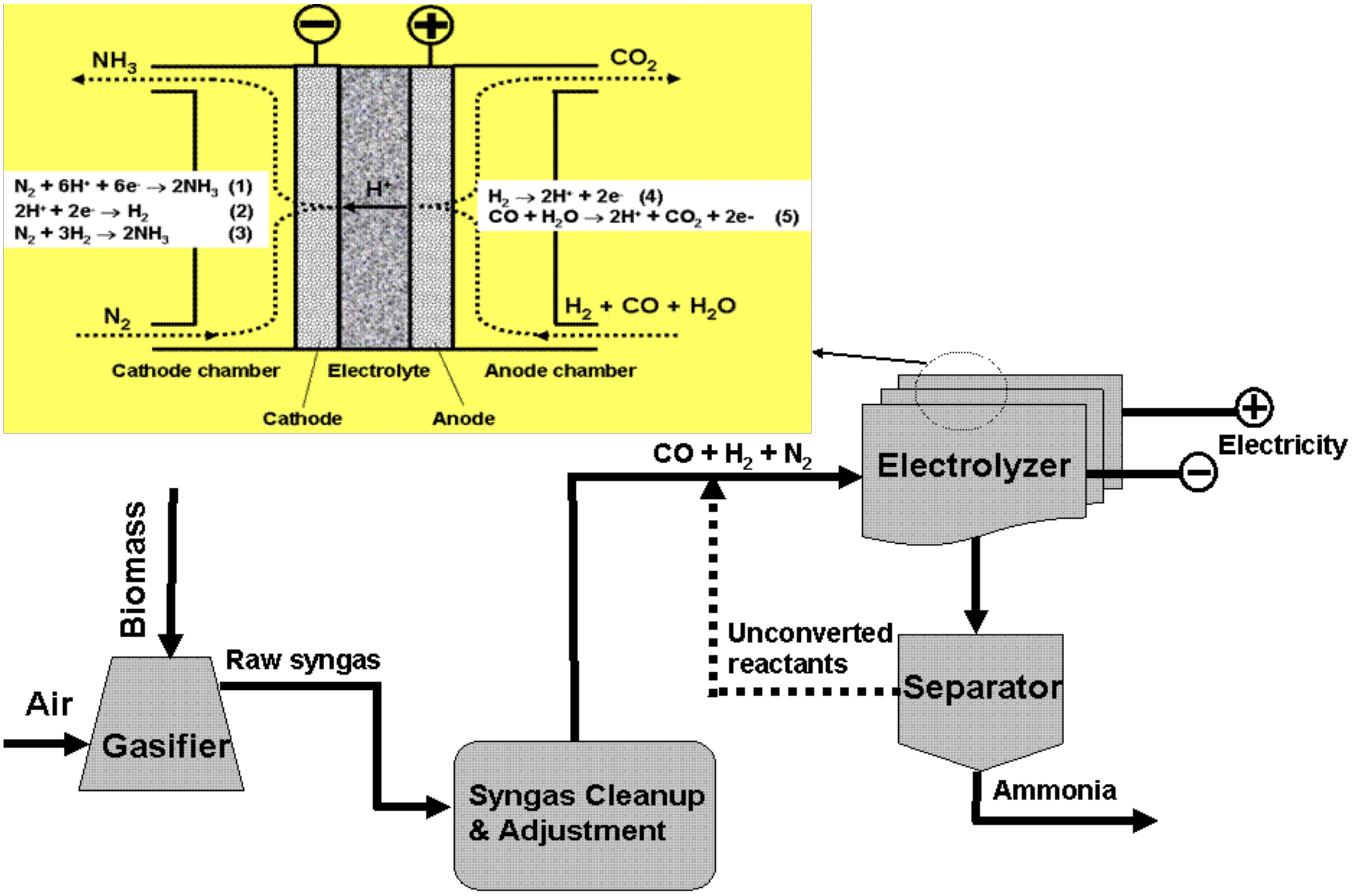
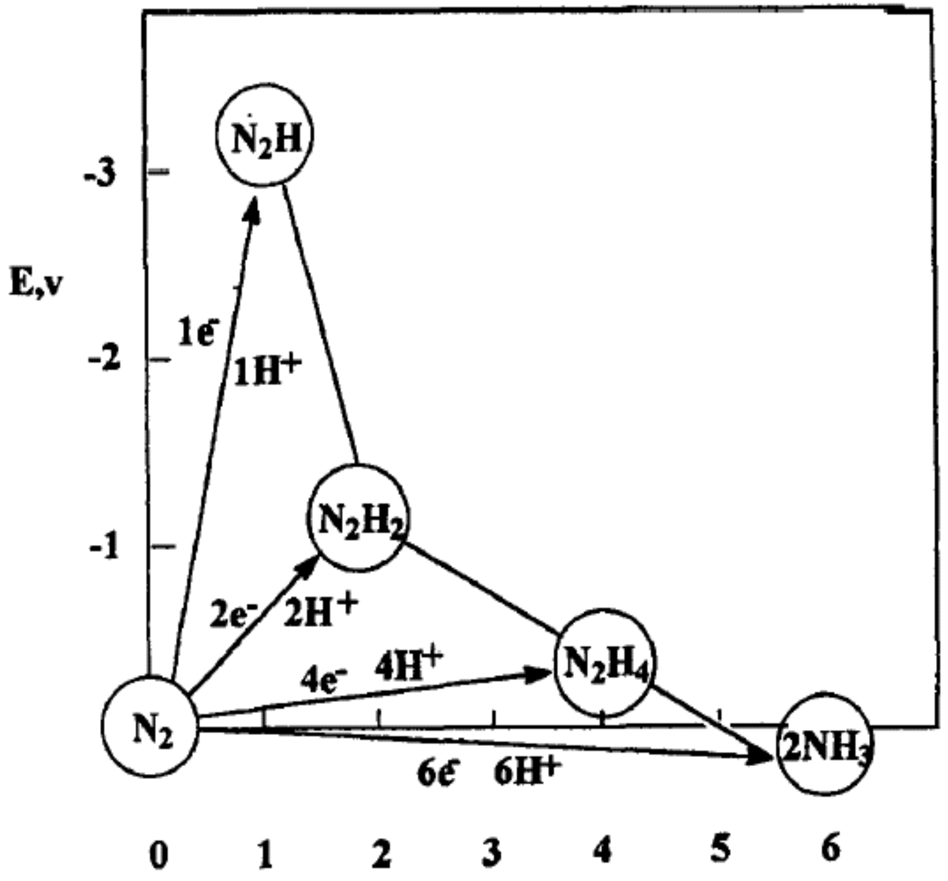
Key advantages of electrolytic ammonia processes

- Replacement of natural gas-derived high-purity hydrogen with syngas and/or other impure (and cheaper) hydrogen source
- Lower reaction pressure means reduced capital cost and increased commercial viability at smaller scales
- Capable of direct utilization of wind and other renewable and/or low-cost electricity
- Could be used as power plant load management strategy

Biosyngas-based ammonia process



Stepwise redox potentials



Chatt J, Camara L M P, Richards R L, *New Trends in the Chemistry of Nitrogen Fixation*, Academic Press, (1980)

- **High ionization potential (14.3 eV) and low electron affinity (0.073 eV) means difficult to reduce and oxidize**
- **Initial electron transfers require higher potential**
- **NH_3 formation via electron–proton addition of dinitrogen is less probable**

Electrocatalysis

Cathode reactions:

Target: $N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$, $E^oN_2/NH_3 = +0.06$ V (1)

Side reaction: $2H^+ + 2e^- \rightarrow H_2$, $E^oH^+/H_2 = 0.0$ V (2)

Possible reaction mechanism

$N_2 \rightarrow N_2$ (adsorbed)

N_2 (adsorbed) → 2 N (adsorbed) slow! 946 kJ/mol disso. energy

N (adsorbed) + e^- + H^+ → NH (adsorbed)

NH (adsorbed) + e^- + H^+ → NH_2 (adsorbed)

NH_2 (adsorbed) + e^- + H^+ → NH_3 (adsorbed)

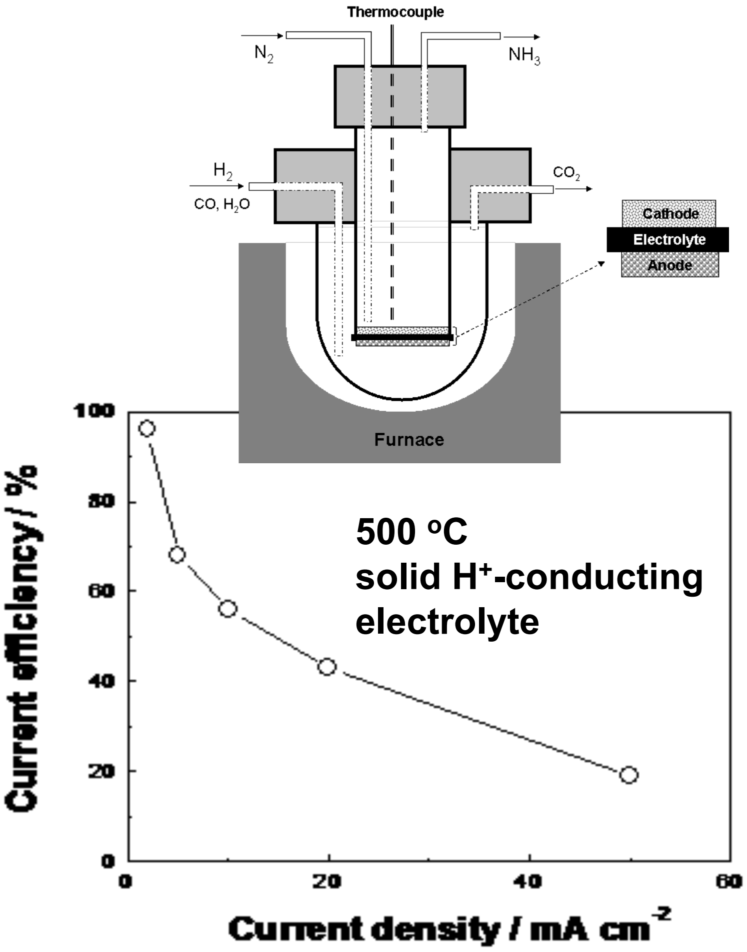
NH_3 (adsorbed) → NH_3

Considerations

- Because dissociative adsorption of N_2 on electrode surface is rate-determining step, high reaction temperature and highly active catalyst are required.
- Because Reaction 2 is kinetically favored, inhibition of H_2 evolution is required for high current efficiency.

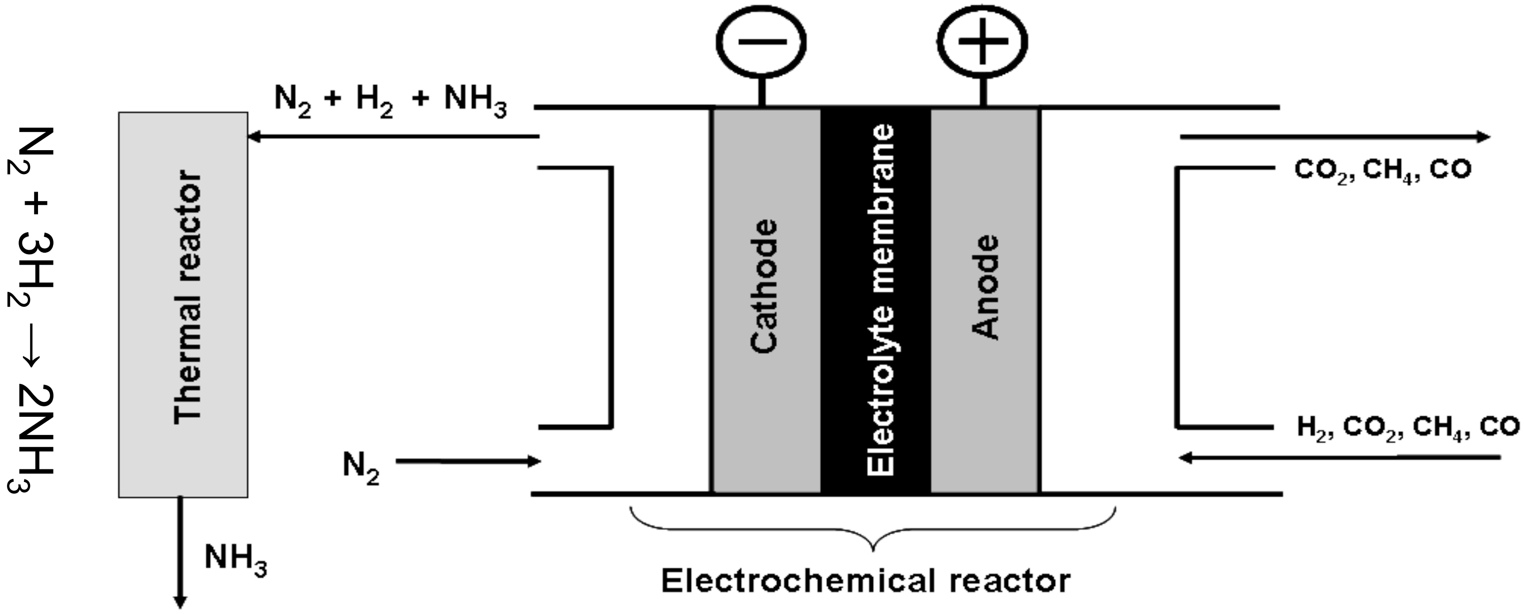
Challenges to direct electrolytic ammonia process

- Low reaction rate (10^{-3}–10^{-2} mmol h^{-1} $g^{-1}_{catalyst}$) and/or low current efficiency.
- Lack of suitable electrolyte systems in 300–500°C temperature range at which ammonia process can be optimized.
- 500°C+ ceramic-based proton conductors and oxygen ion-conductors are available, but difficult to scale up.



500 °C
solid H^+-conducting electrolyte

Integrated electrochemical–thermal process



- Enables scale-up based on state-of-the-art technologies
- Eliminates electrochemical-only problem of evolved H_2 side product
- Enables optimization of each of two individual process steps

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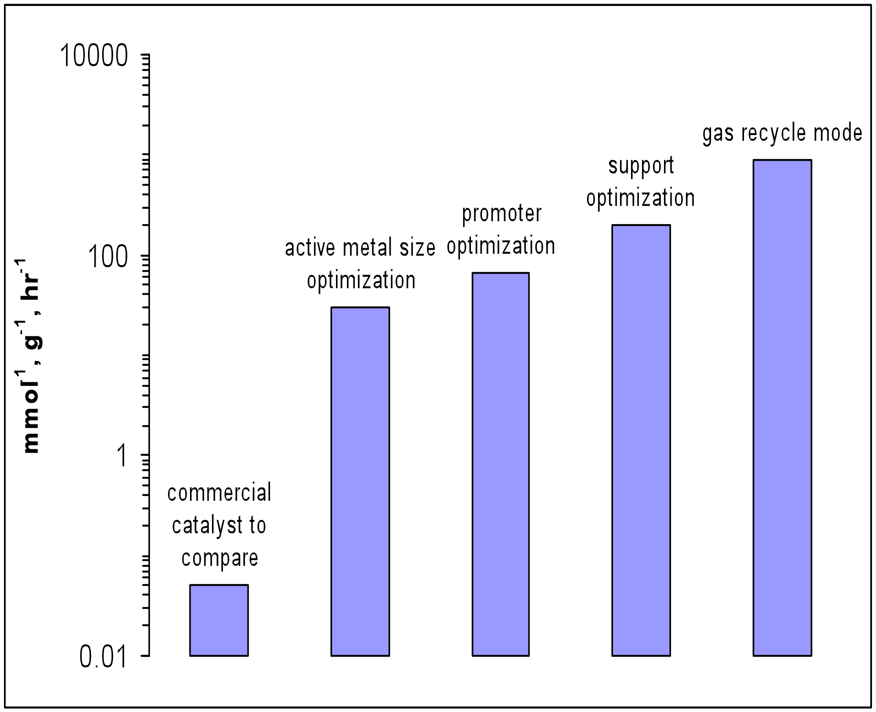
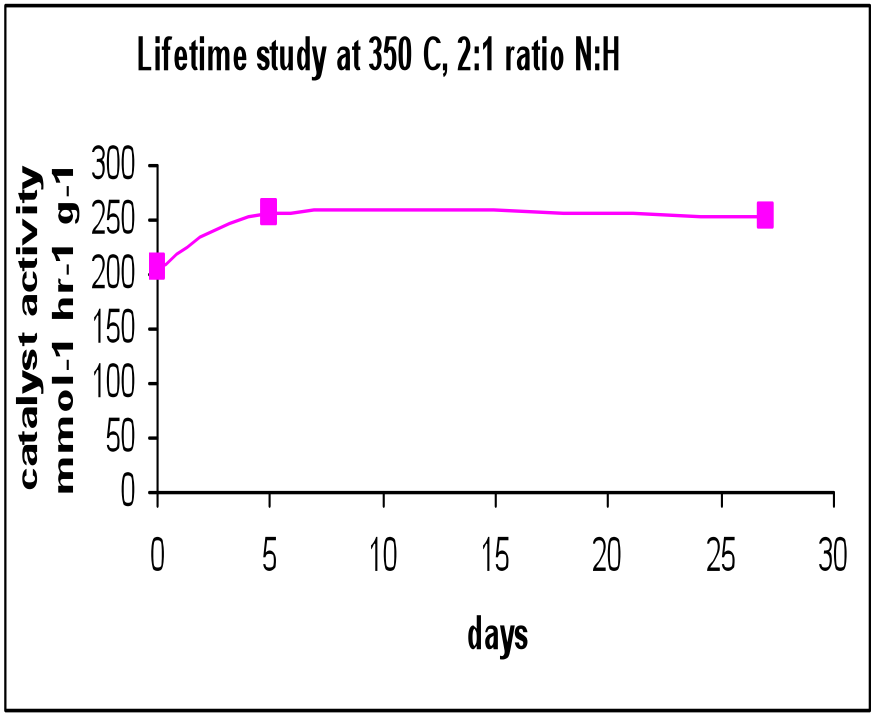
Key developments

- Low-temperature ambient-pressure ammonia catalyst
- Electrochemical hydrogen purification process
- Integration of electrochemical and thermal process
- Demonstration of electrolysis scale-up using a 200-W electrolyzer stack

Catalyst activity improvement

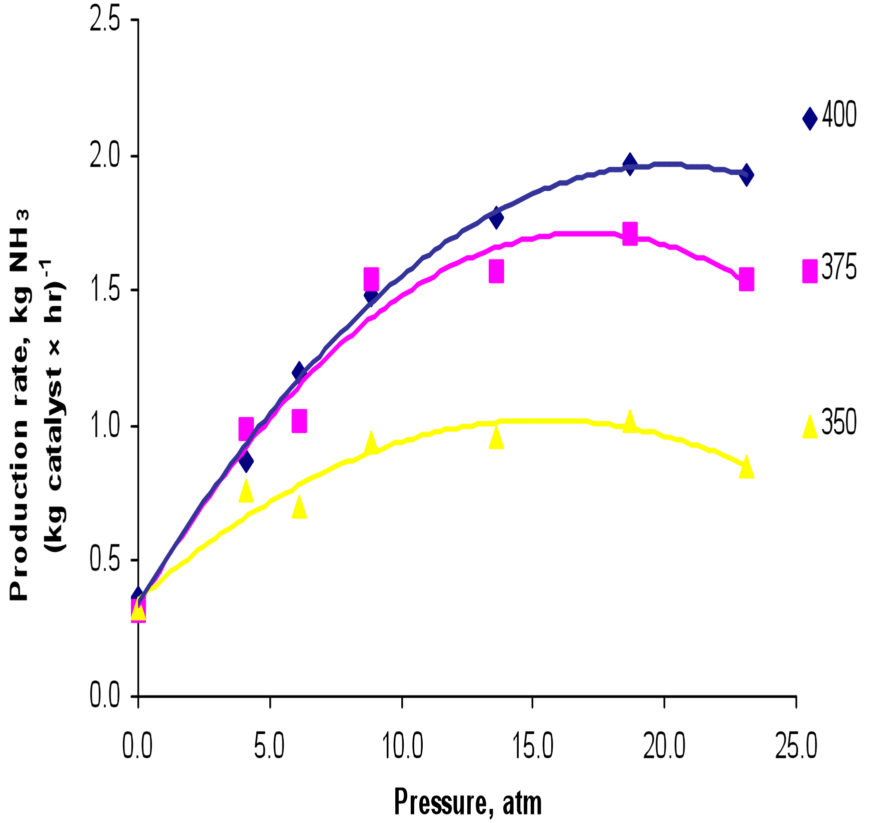




- •Highly active catalysts developed via nanofabrication, support optimization, and surface modification
- •Good catalyst activity durability demonstrated at ambient pressure and 350°C

EERC thermal catalysis process

- **Mild operating conditions:**
  - 250-375°C
  - 14-20 atm
- **High catalyst activity**: 2.0 kg NH_3/(kg catalyst-hr) 5 times higher than Haber
- **Lower energy**: 10% less input energy than Haber
- **No methane build up** owing to no methanation reactor
- **Higher catalyst oxygen tolerance**



Electrochemical H_2 purification

Anode reaction:

$H_2 \rightarrow 2H^+ + 2e^-$

$E^o = 0\ V$

Cathode reaction:

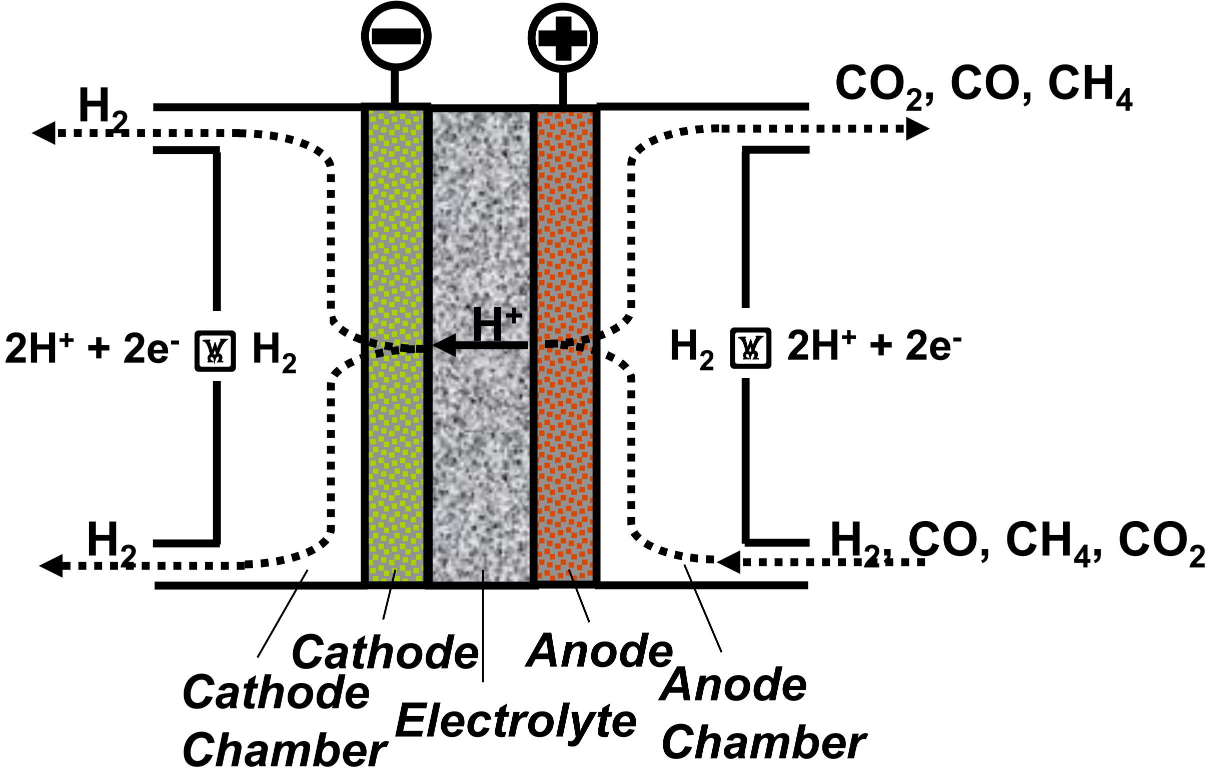
$2H^+ + 2e^- \rightarrow H_2$

$E^o = 0\ V$

Total reactions:

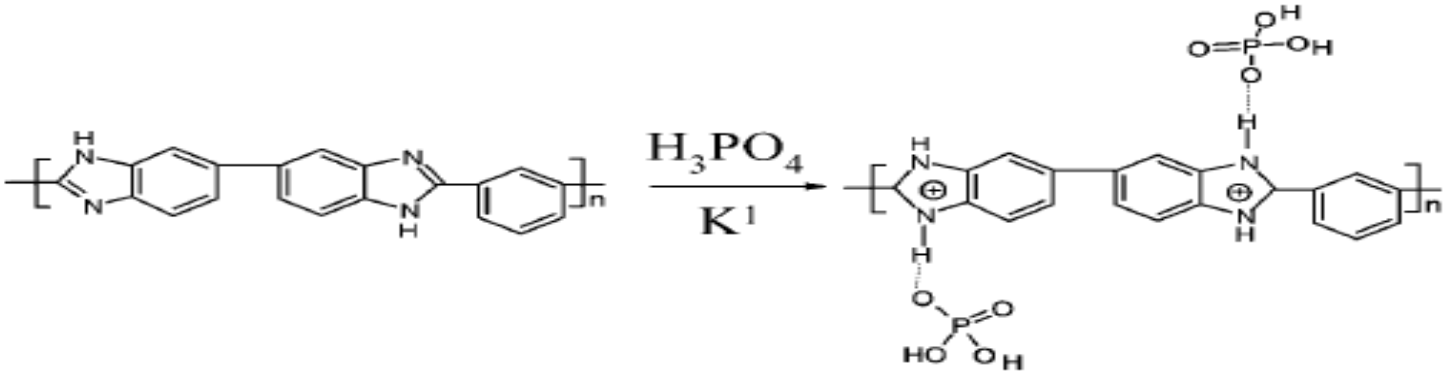
$H_2 \rightarrow H_2$

$\Delta E^o = 0\ V$



- High-purity H_2 obtained at cathode.
- Low energy consumption.
- Anode catalysts must have CO tolerance.

Polybenzimidazole (PBI)

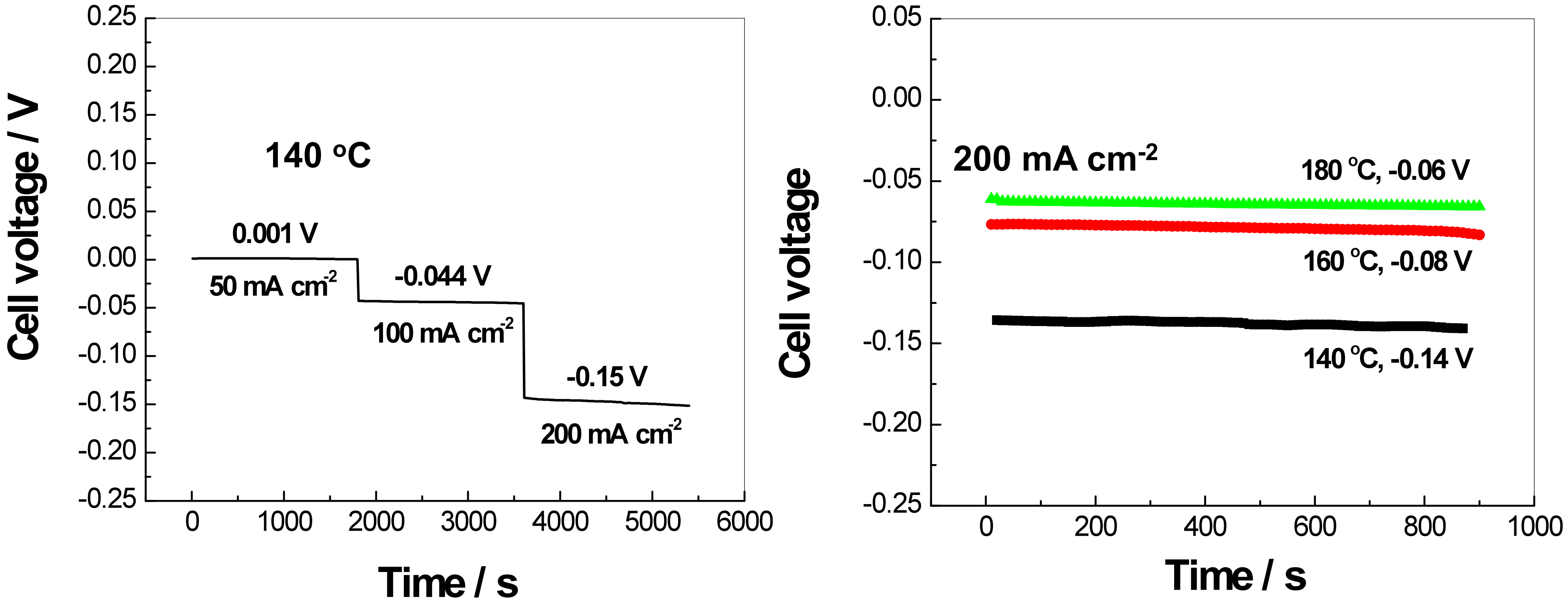


- High working temperature (140°–200°C) increases CO tolerance of Pt-based catalysts to 3% at around 180°C.
- High proton conductivity (~0.1 S/cm^{-1}) decreases energy consumption.
- Scalable for kW-scale PEMFC application.
- Duration has been demonstrated for high-temperature application (20,000 hours of operation with reformate).
- Low gas crossover.

Hydrogen purification energy consumption

Pt/C cathode, 60 sccm N_2

H_3PO_4-PBI/ Pt/C anode, 180 sccm simulated syngas



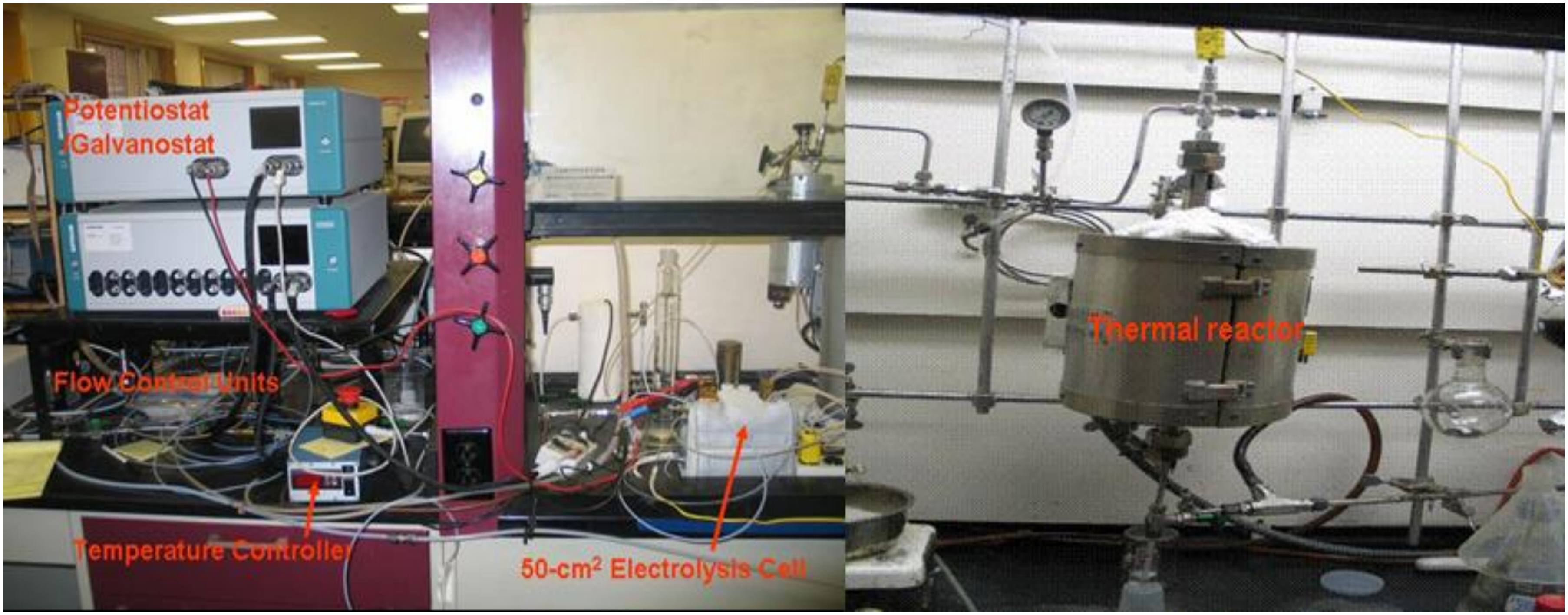
- **Low energy consumption: At 200 mA/cm^{-2}, 1.6–3.8 kWh (@180–140°C) to produce 1 kg H_2.**
- **At $0.05/kWh electricity price, $0.10–$0.20 per kg H_2.**

Purification results

Temperature, ^{O}C	Current Density, mA/cm^{-2}	Cathode Gas Composition Using N_2 as Carrying Gas		Current Efficiency		Crossover of H_2 Using Reformate, sccm
		H_2	Reformate	H_2	Reformate	
140	200	50.6% H_2 + 49.4% N_2	49.7% H_2 + 50.3% N_2	94.3%	92.6%	–
160	200	–	51.9% + 48.1% N_2	–	96.6%	–
180	200	–	50.9% H_2 + 49.1% N_2	–	94.8%	–
180	0	–	0.04% H_2 + 99.96% N_2	–	–	0.02

- At 200 mA/cm^{-2}, only H_2 detected at cathode.
- Current efficiency for H_2 purification is very high.
- At open circuit potential, only H_2 can crossover the membrane, while CO_2, CO, and CH_4 are blocked.

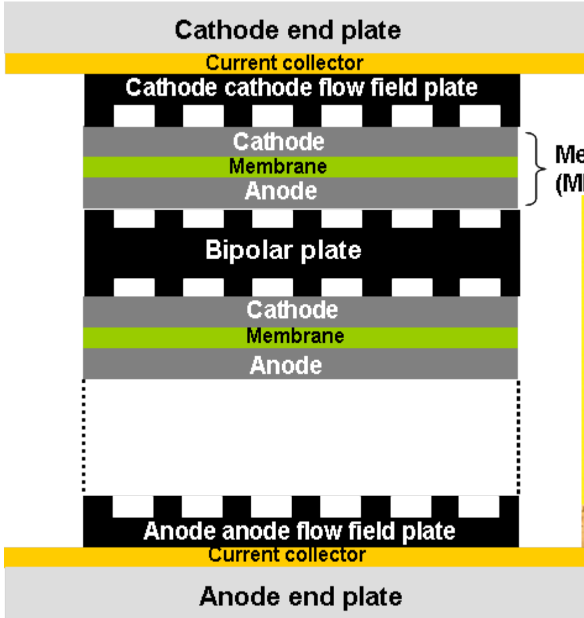
Process demo using 20-W electrolyzer + tube thermal reactor

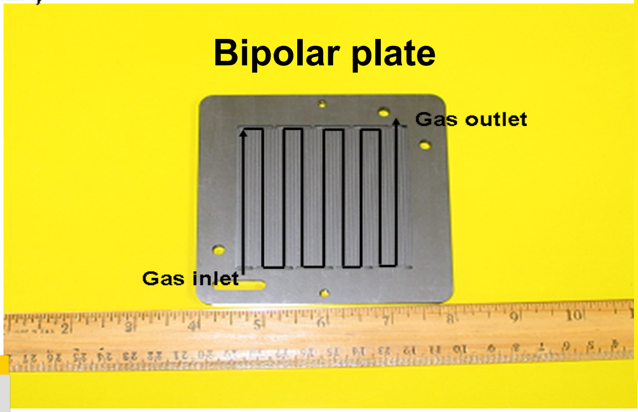


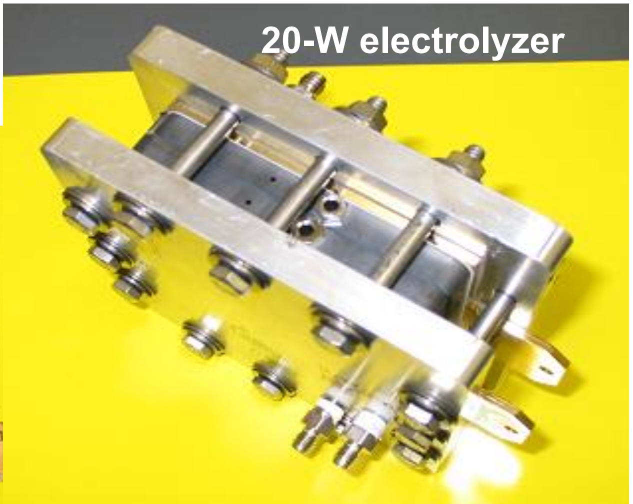
- Operating conditions
  - Electrochemical cell: 180°C, 10 A (200 mA cm^{-2})
    Anode syngas: 76% H_2/2% CO/2% CH_4/20% CO_2
  - Thermal reactor: 400°C, N_2(input):H_2 (generated)=2:1
- Electrochemical cell voltage measured: 0.14–0.17 V
- Ammonia production rate
  - Single-pass-through: 153 mmol NH_3 hr^{-1} g^{-1}
  - Gas recycle: 389 mmol NH_3 hr^{-1} g^{-1}

Process optimization using 200-watt electrolyzer

- Design and fabrication of components for 200-W stack completed
- Membrane–electrode assembly scaled up
- Process optimization in the stack underway


Cathode end plate
Current collector
Cathode cathode flow field plate
Cathode
Membrane
Anode
Membrane-electrode-assembly (MEA)
Bipolar plate
Cathode
Membrane
Anode
Anode anode flow field plate
Current collector
Anode end plate


Bipolar plate


20-W electrolyzer

Per-ton biosyngas-based ammonia cost projection – 500-lb/day production capacity

	Initial	*August 09*	*January 010*
Syngas price	\$6/MMBTU[1]	\$6/MMBTU	\$6/MMBTU
Electricity price	\$0.05/kWh[2]	\$0.05/kWh	\$0.05/kWh
Cost of electricity[3]	**\$322**	**\$240**	**\$120**
Cost of syngas input	\$142	\$142	\$142
Capital cost	\$21	\$21	\$21
O & M cost	\$20	\$20	\$20
Cost of N_2	\$12	\$12	\$12
Total cost	**\$517**	**\$435**	**\$315**

[1] ***DOE 2010 target is \$6/Million Btu (MMBTU)***

[2] ***Kilowatt hour***

[3] ***Electricity consumption of 6,450 kWh/ton ammonia (initial) vs 4,800 kWh/ton (August 09) vs 2,400 kWh/ton (current)***

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Summary

- An integrated electrochemical–thermal ammonia process has been developed and demonstrated using simulated syngas.
- The electro–thermal process enables scale-up based on integration with state-of-the-art syngas/reformate technologies.
- Preliminary economic analysis indicates commercial competitiveness achievable with \$6/MMBtu syngas and \$0.05/kWh electricity.

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Acknowledgment

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