# NH3 from Renewable-source Electricity, Water, and Air: Technology Options and Economics Modeling

**Ammonia Fuel Association**
**21 – 24 September 2014**
**Des Moines, Iowa USA**

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*Rev: 29 Sep 14*

Mendenhall Glacier, Juneau, AK

June ‘71

Mendenhall Glacier,  Juneau,  AK

10 October 10

**Mendenhall Glacier, Juneau, AK**
**10 October 10**

# Rapid climate change

Spruce bark beetle kill, Alaska

Shishmaref, Alaska

Winter storms coastal erosion

**35,000 walrus have come ashore in NW Alaska: usual sea ice is gone**

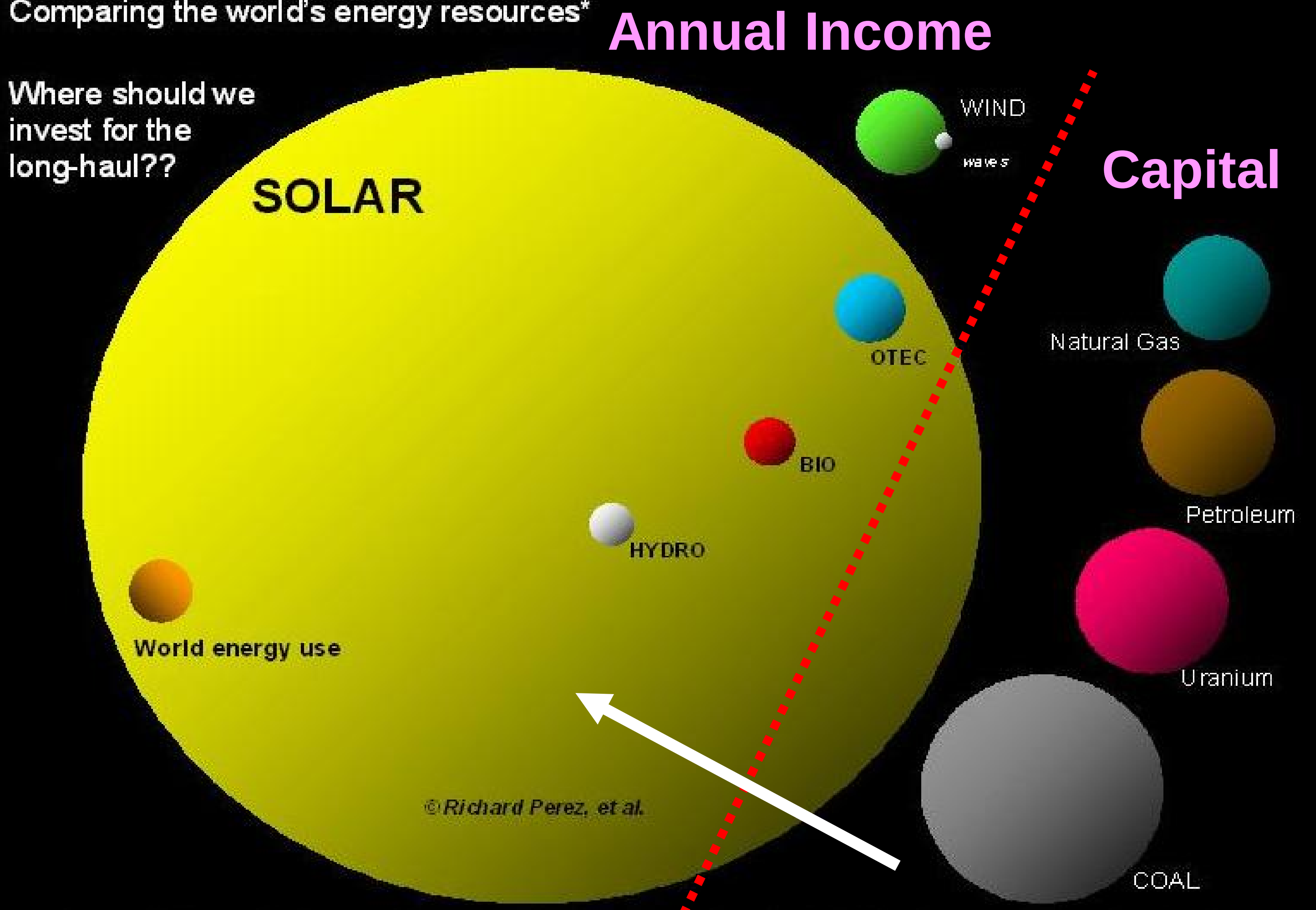
35,000 walrus stranded in NW Alaska: their usual sea ice is gone

Baby walrus are often crushed during stampedes ashore

# MUST Run the World on Renewables – plus Nuclear ?

- Climate Change
- Ocean acidification
- Sea level rise
- Demand growth
- Water for energy
- War
- Depletion of Oil and Gas and Coal
- Only Source of Income:
    - Sunshine, tides
    - Spending our capital

Comparing the world's energy resources*




*yearly potential is shown for the renewable energies. Total reserves are shown for the fossil and nuclear "use-them, lose-them" resources. Word energy use is annual.

# Running the World on Renewables: Alternatives to Electricity for Transmission and Low-cost Firming Storage of Stranded Renewables as Hydrogen and Ammonia Fuels via Underground Pipelines

*ASME Energy Sustainability and Fuel Cell Science*
*30 June – 2 July 2014, Boston*

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# *Trouble with Renewables*

- Diffuse, dispersed:  gathering cost
- Richest are remote:  “stranded”
  - High intensity
  - Large geographic extent
- Time-varying output:
  - “Intermittent”
  - “Firming” integration + storage required
- Distributed AND centralized

# *Trouble with Renewables: Big Three*

1. Gathering and Transmission
2. Storage: Annual-scale firming → dispatchable
3. Integration
   - Extant energy systems
   - Electricity grid
   - Fuels:  CHP, transportation, industry

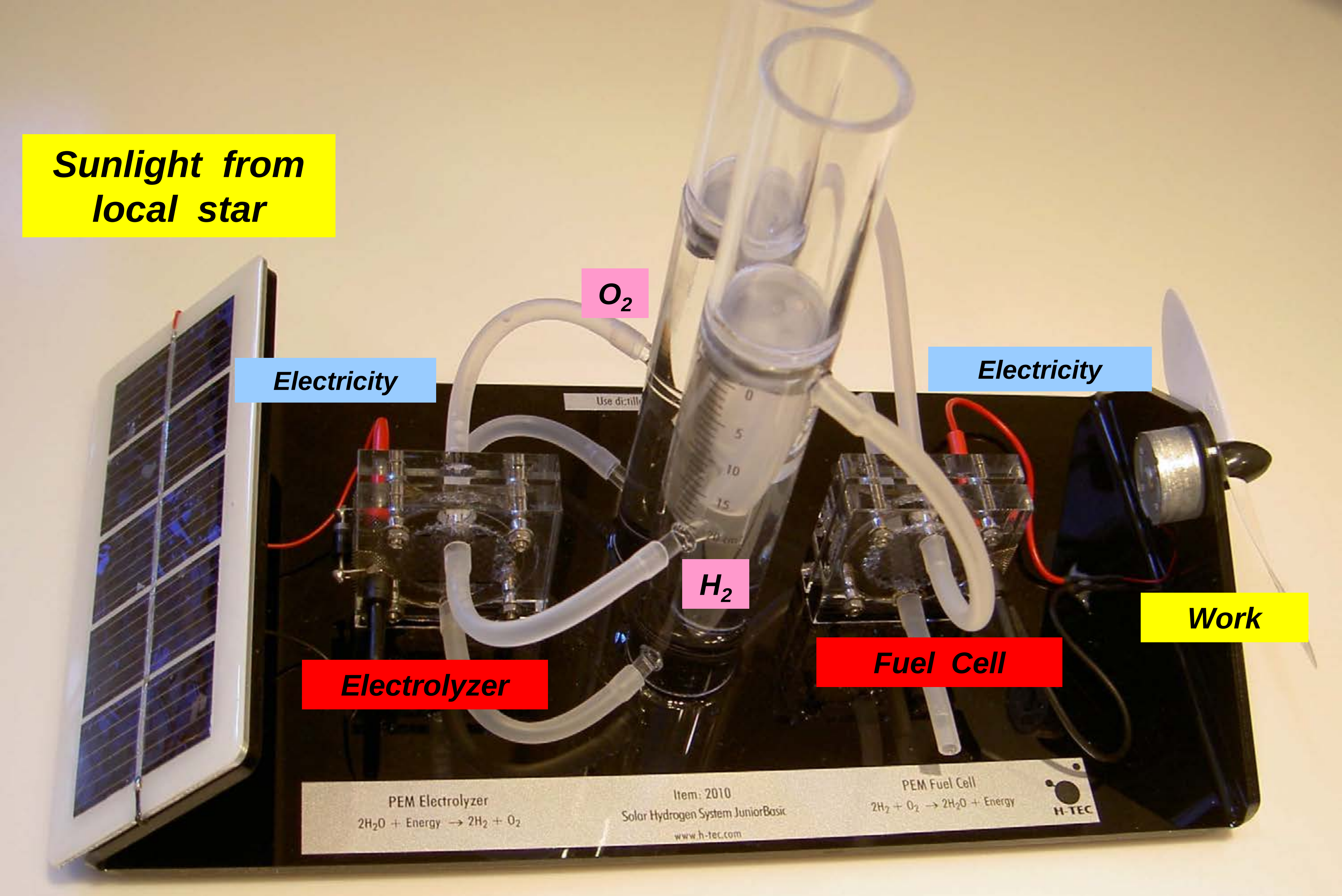
# *Beyond "Smart Grid"*

- Next big thing;  panacea
- Primarily DSM
- More vulnerable to cyberattack ?
- Adds no physical:
  - Transmission, gathering, distribution
  - Storage
- Run the world on renewables ?
- Must think:
  - Beyond electricity
  - Complete energy systems
  - ALL energy

# *“Transmission”*

- **Electrofuels**
  - **CHP on-site:  Combined Heat and Power**
  - **Transport**
  - **Industrial**
- **Renewable-source electricity**
- **Underground pipelines**
- **Carbon-free fuels: hydrogen, ammonia**
- **Low-cost storage:**

  **$ 0.10 – 0.20 / kWh  capital**
- **RE systems, GW scale**

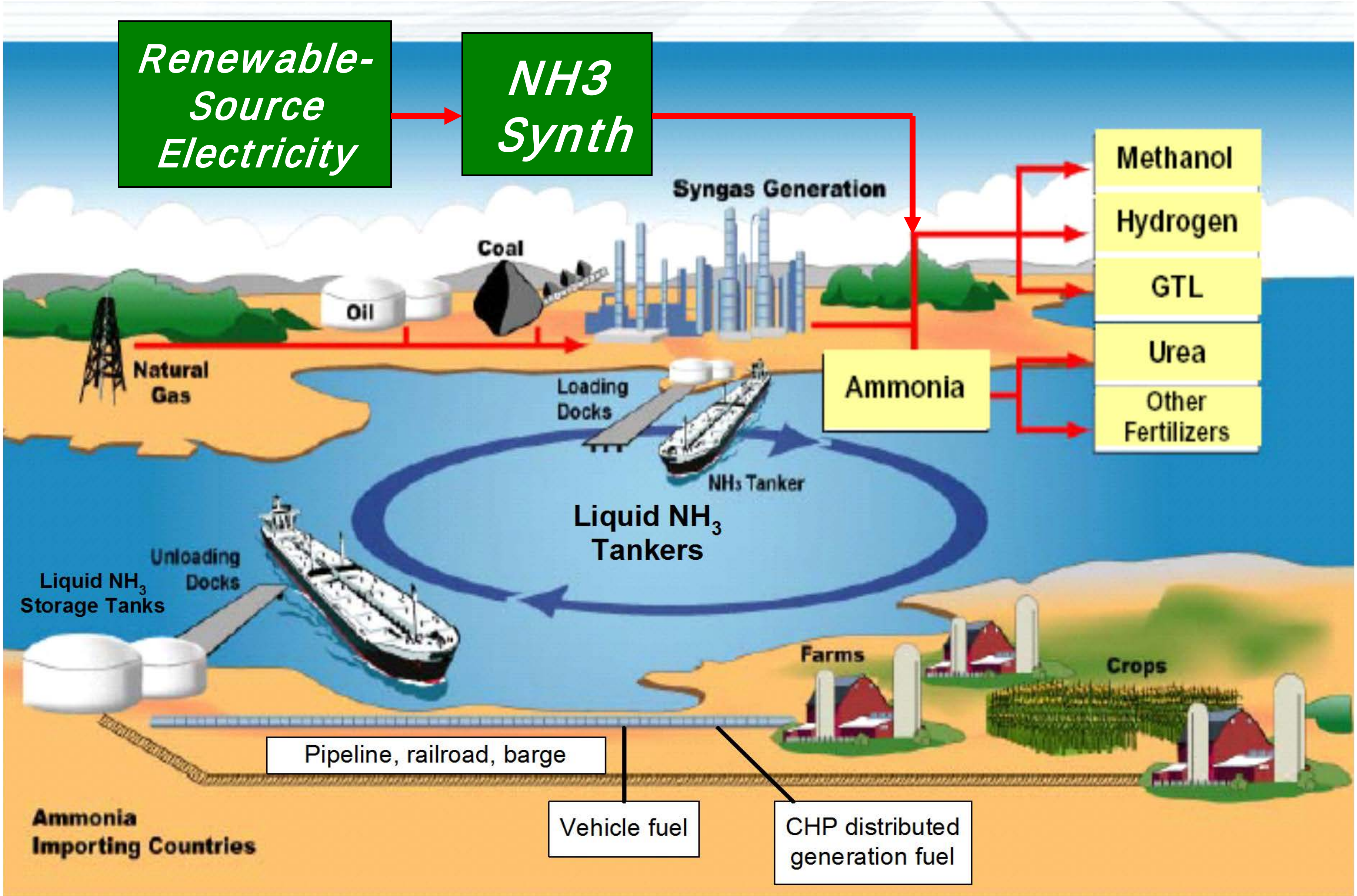



# Solar Hydrogen Energy System

# *Landscape: RE-source NH3*

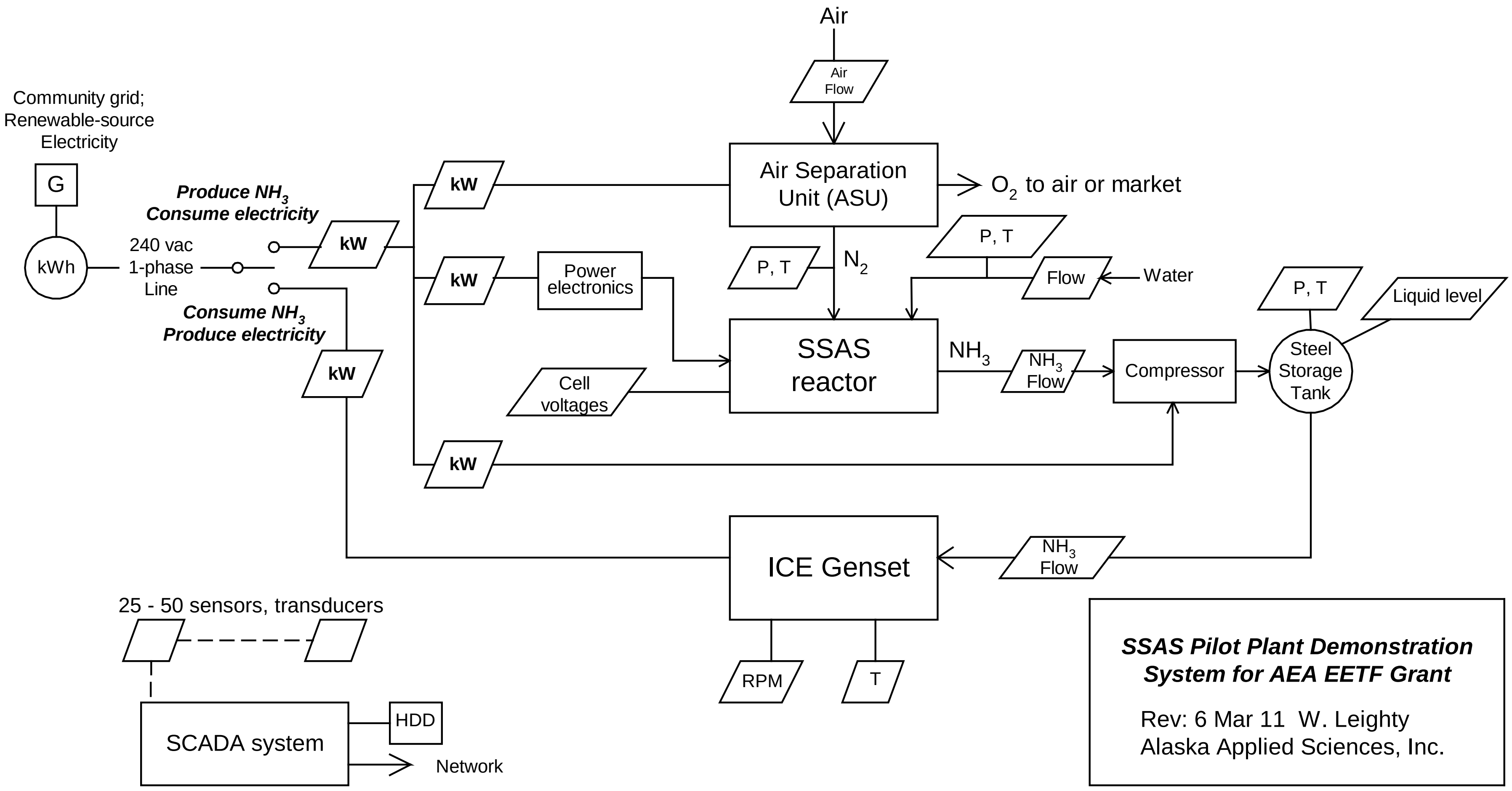
- Alaska demo project: AASI
- Complete RE systems:
  - Generation, harvesting
  - Gathering + Transmission
  - Annual-scale firming storage
  - Integration: distribution + end-use
- Artificial Photosynthesis: UK, July '14
- Ag Ventures Alliance, Iowa: Wind → NH3 study
- Synthesis tech survey
  - From H2
  - From electricity
- ICE gensets conversion to NH3: demand demo

ARCTIC OCEAN
CHUKCHI SEA
BEAUFORT SEA
GULF OF ANADYR
CHUKOTK
RUSSIA
UNITED STATES
FAR NORTH
Barrow
Wainwright
Point Hope
Prudhoe Bay
Deadhorse
Colville River
Umiat
Noatak
Noatak River
Kotzebue
Noorvik
Selawik
GATES OF THE ARCTIC NAT'L PARK & PRESERVE
Anaktuvuk Pass
ARCTIC NATIONAL WILDLIFE REFUGE
BROOKS RANGE
Arctic Village
ARCTIC CIRCLE
Bettles
Coldfoot
Uelen
Lavrentiya
Provideniya
Little Diomede
Shishmaref
Wales
Teller
Taylor
Pilgrim Springs
Gambell
Savoonga
ST. LAWRENCE ISLAND
Nome
Council
White Mountain
Huslia
U.S.A. ALASKA
CANADA YUKON
Fort Yukon
Nulato
Unalakleet
St. Michael
Galena
Yukon R.
Tanana
Rampart
Stevens Village
Manley Hot Springs
Central
Circle
Chena Hot Springs
INTERIOR
Fairbanks
North Pole
Nenana
YUKON-CHARLEY RIVERS NAT'L PRESERVE
Eagle
Boundary
Dawson City
Chicken
Delta Jct.
DENALI NAT'L PARK & PRESERVE
Kantishna
Healy
MT. McKINLEY
Cantwell
ST. MATTHEW ISLAND
Emmonak
Scammon Bay
Hooper Bay
Saint Marys
Holy Cross
KUSKOKWIM MTNS.
McGrath
Mekoryuk
NUNIVAK ISLAND
Bethel
Aniak
Kuskokwim River
BERING SEA
ALASKA RANGE
Paxson
Tok
Northway
PRIBILOF ISLANDS
ST. PAUL ISLAND
ST. GEORGE ISLAND
KISKA ISLAND
SOUTHWEST
Quinhagak
Goodnews Bay
TOGIAK NAT'L WILDLIFE REFUGE
Wood-Tikchik System
LK. CLARK NAT'L PARK & PRESERVE
Lake Clark
Talkeetna
Willow
Houston
Big Lake
Wasilla
Sutton
Lake Louise
Gakona Jct.
Glennallen
Nabesna
Beaver Creek
Anchorage
Palmer
Copper Center
CHUGACH MTNS.
Chitina
Carmacks
Ross River
N.W. TERRITORY
YUKON
Dillingham
Nushagak River
Iliamna
Iliamna Lake
Kenai
Soldotna
Whittier
Valdez
Kennicott
McCarthy
PRINCE WILLIAM SOUND
Kluane Lake
Lake Laberge
Naknek
King Salmon
Ninilchik
Anchor Pt.
Homer
Seldovia
COOK INLET
Seward
Cordova
Destruction Bay
KLUANE NAT'L PARK
Haines Junction
Whitehorse
KATMAI NAT'L PARK & PRESERVE
KENAI FJORDS NAT'L PARK
WRANGELL-ST. ELIAS NAT'L PARK & PRESERVE
ALEUTIAN ISLANDS
ANIAKCHAK NAT'L MONUMENT & PRESERVE
Port Lions
Kodiak
KODIAK ISLAND
Old Harbor
KODIAK NATIONAL WILDLIFE REFUGE
SOUTHCENTRAL
Yakutat
White Pass Summit
Carcross
Watson Lake
BRITISH COLUMBIA
Dutch Harbor
Unalaska
Akutan
False Pass
Cold Bay
King Cove
Chignik
Sand Point
GULF OF ALASKA
Haines
Skagway
GLACIER BAY NAT'L PARK & PRESERVE
Gustavus
Auke Bay
Juneau
Elfin Cove
Pelican
Hoonah
Tracy Arm
Tenakee
Angoon
Stikine River
PACIFIC OCEAN
Sitka
Kake
Petersburg
INSIDE PASSAGE
Wrangell
Hyder
Stewart
MISTY FIORDS NAT'L MONUMENT WILDERNESS
Hollis
Ketchikan
Metlakatla
Prince Rupert




KBR
Energy and Chemicals


**Proton Ventures BV, Netherlands**
**www.protonventures.com**




**PROJECT: Complete RE – $NH_3$ Synthesis + Storage System**

- **> NH3 synthesis from RE electricity, water, air ($N_2$)**
- **> Liquid $NH_3$ tank storage**
- **> Regeneration + grid feedback**
- **> SCADA instrumentation → UAF - ACEP**

# *Alaska NH3 Pilot Plant Budget*

| | |
|---|---|
| EETF via AEA | $ 750 K |
| Technology in-kind | $ 100 K |
| WindToGreen in-kind | $ 100 K |
| AASI in-kind | $ 50 K |
| TOTAL | $ 1 M |

| | |
|---|---|
| EETF | Emerging Energy Technology Fund, State of Alaska |
| AEA | Alaska Energy Authority, State of Alaska |
| AASI | Alaska Applied Sciences, Inc. |

# Landscape Survey: RE-source NH3

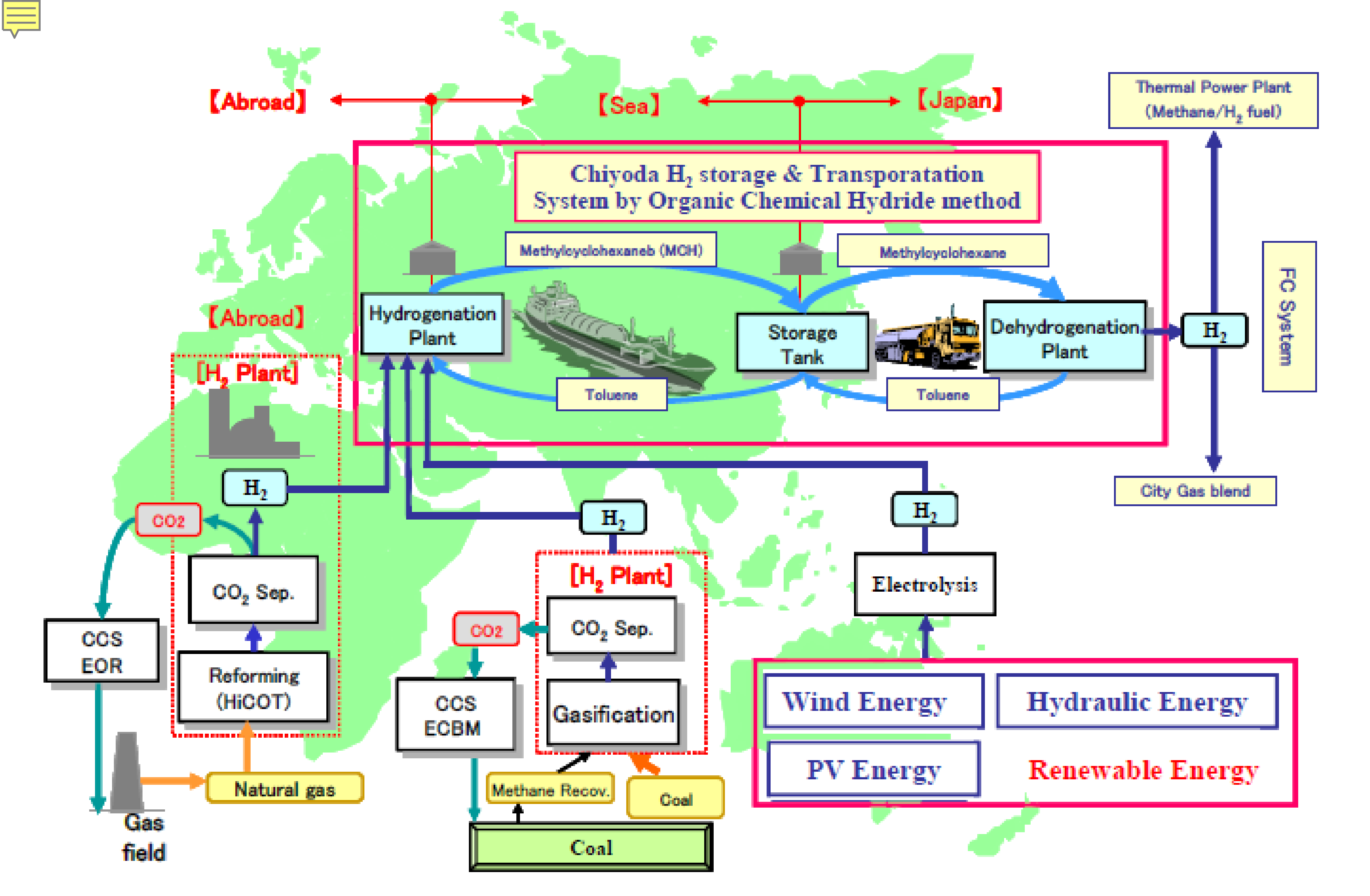
- WindToGreen, LLC  technology survey
- Researchers always want “Better catalysts”
- New methods, pathways, to NH3 synthesis
- All “Non-Haber” tech is at TRL 1-3
- Electrolysis + Haber-Bosch (EHB) is lowest risk
- Long-term, costly effort ahead for RE-NH3
- High cost of RE-NH3: competition, C-tax ?

# *Landscape: RE-source $NH_3$*

– Sources: Electricity or Hydrogen ?
– Markets:
  - Transportation Fuel
  - Ag Fuel
  - N-fertilizer
  - Distributed Generation (DG) Fuel
  - Industrial Fuel + Feedstock
  - “Run World on Renewables”

# *RE Systems: Carriers and Storage Strategies*

- Electricity
- Gaseous Hydrogen (GH2)
- Liquid Hydrogen (LH2)
- Anhydrous Ammonia (NH3)
- Toluene (C7H8) ←→
  Methylcyclohexane (C7H14)
- Artificial Photosynthesis (AP)




**C-emissions-free Hydrogen transport and storage: Chiyoda Chemical, Japan**

**Toluene (C7H8) ←→ Methylcyclohexane (C7H14)**

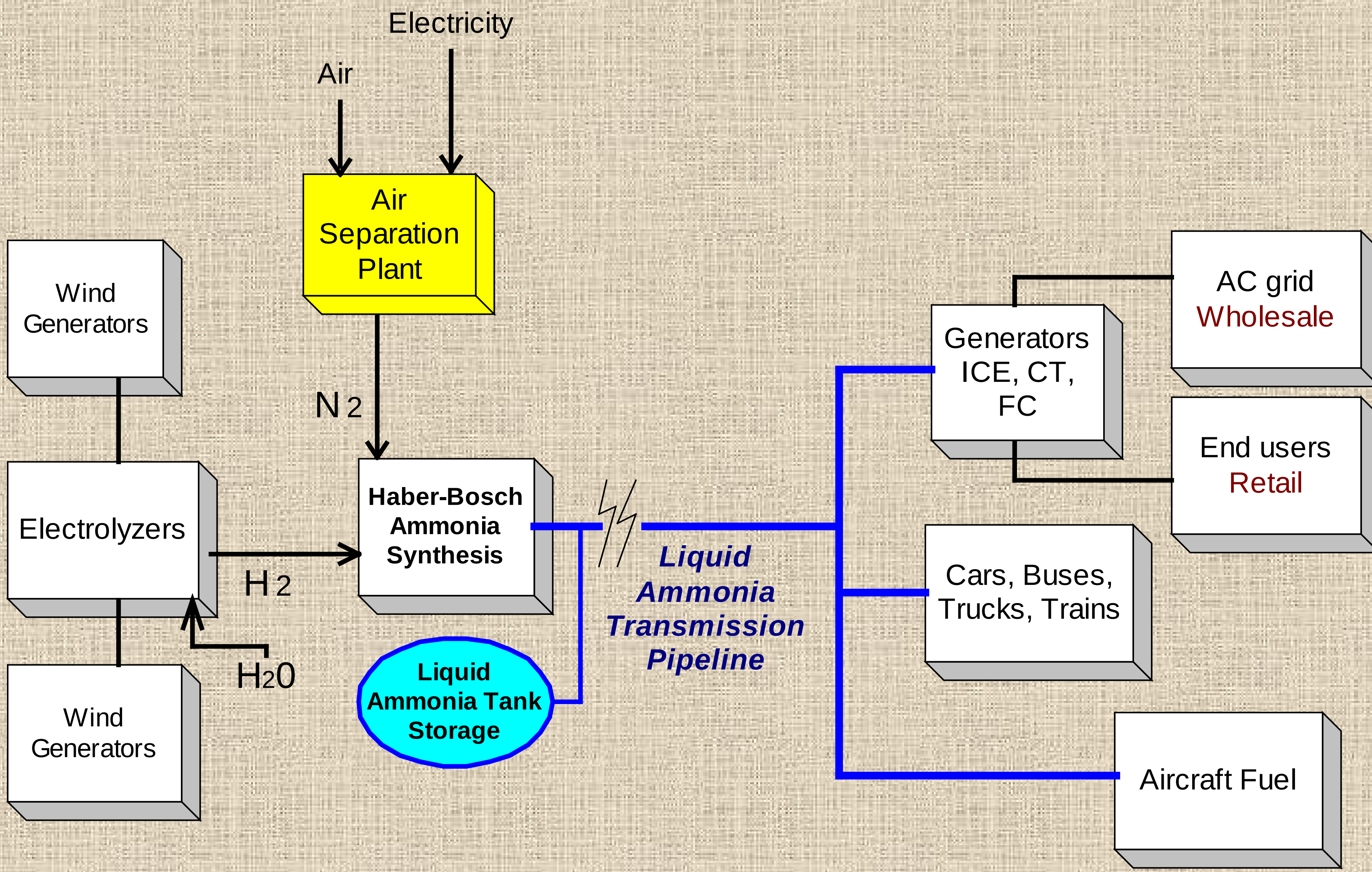
# *RE Systems: Carriers and Storage Strategies*

- Electricity
- Gaseous Hydrogen (GH2)
- Liquid Hydrogen (LH2)
- Anhydrous Ammonia (NH3)
- Toluene (C7H8) ←→ Methylcyclohexane (C7H14)
- Artificial Photosynthesis (AP)

**Global Artificial Photosynthesis Project**
**The Royal Society, Chicheley Hall, UK July 8 – 10, 2014**
**Tom Faunce, Australia National University, Convenor**
**Leighty for NH3 Fuel Association: "What Shall We Do With The Photohydrogen?"**

# Chicheley Hall, The Royal Society, UK

# *RE Ammonia Transmission + Storage Scenario*

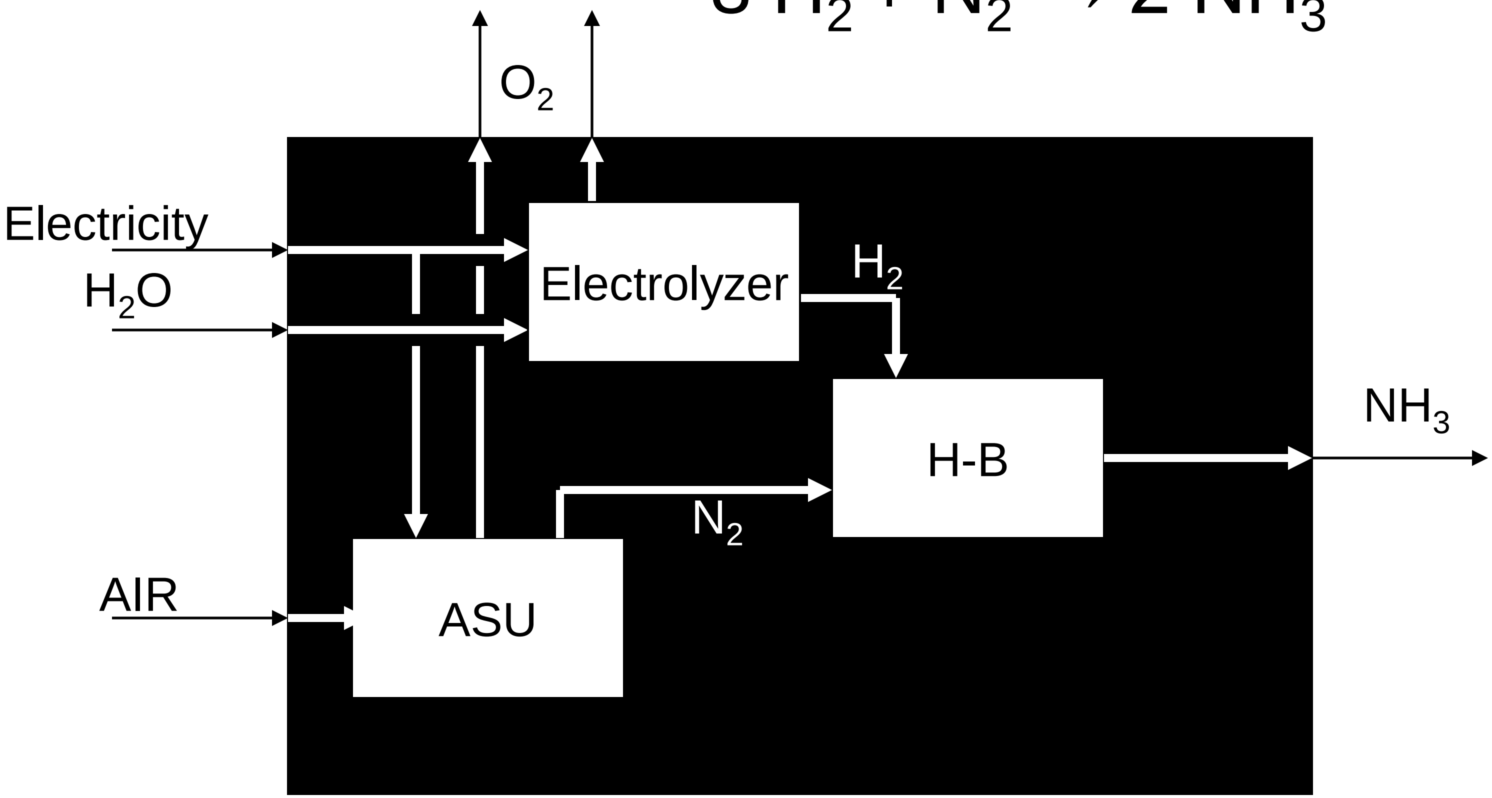


# Norsk Hydro Electrolyzers 2 MW each

Ammonia from hydrogen from zero-cost off-peak hydro

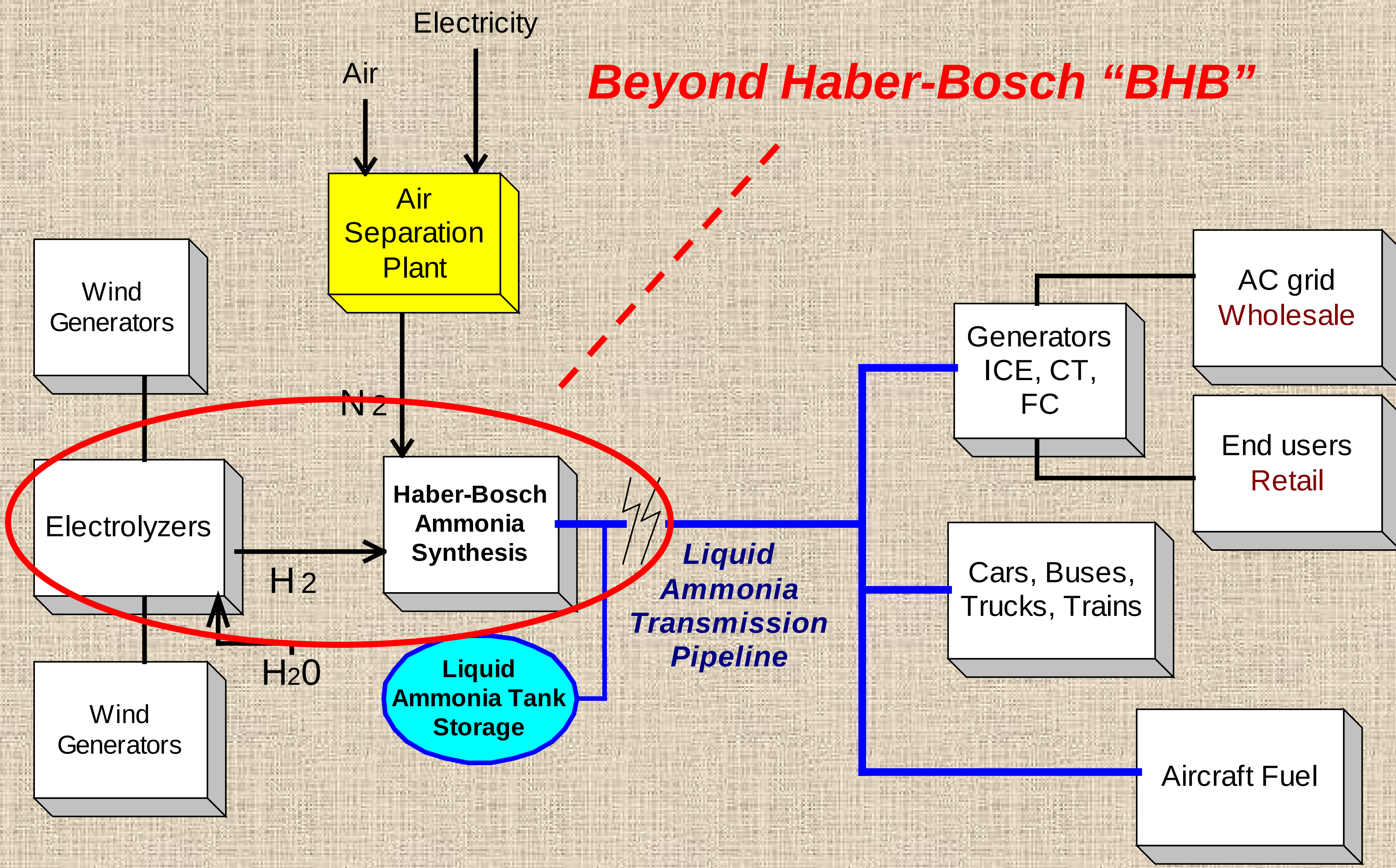
# Inside the Black Box:
# HB Plus Electrolysis

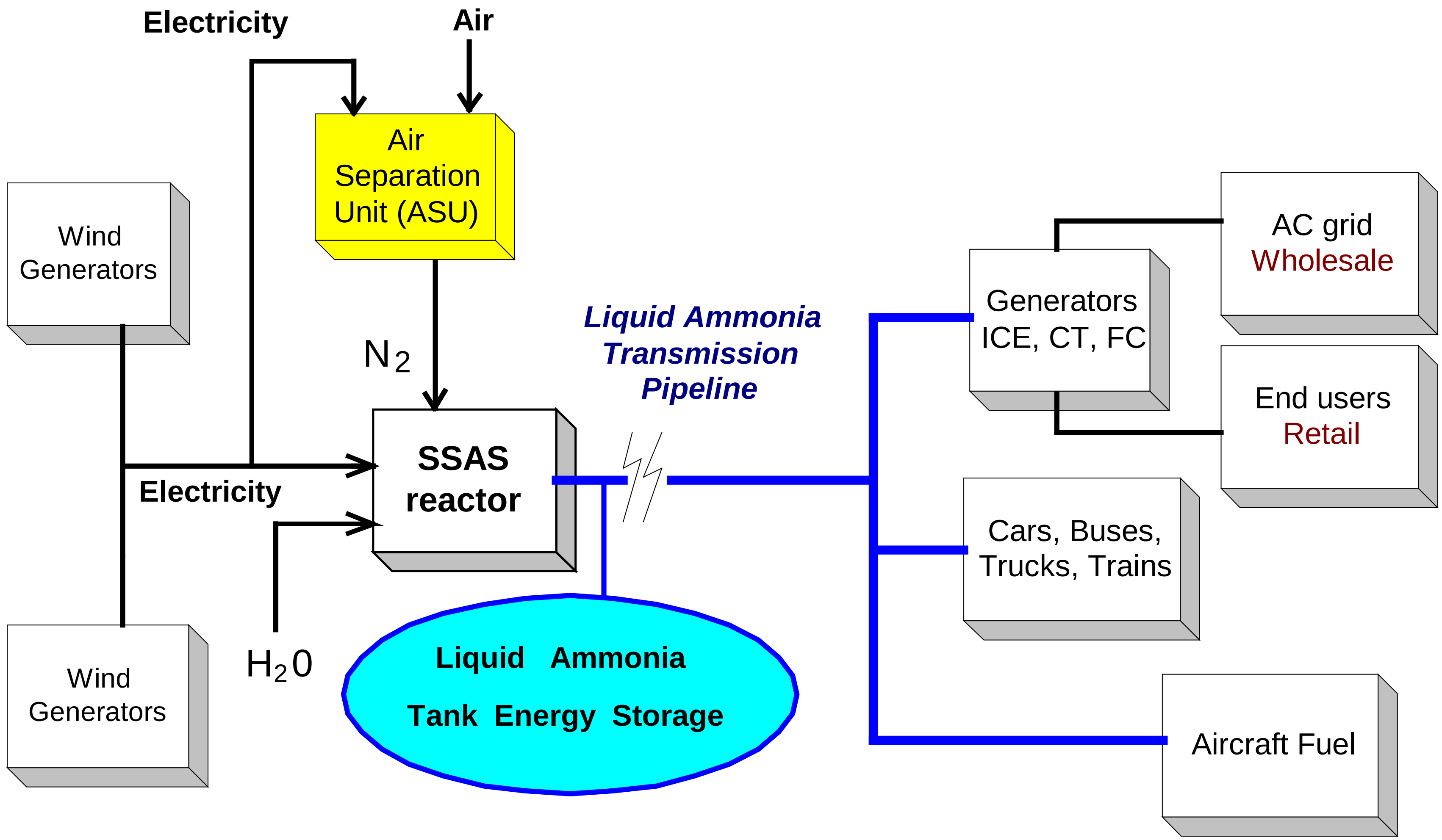
$$3\ H_2O \rightarrow 3\ H_2 + 3/2\ O_2$$
$$3\ H_2 + N_2 \rightarrow 2\ NH_3$$



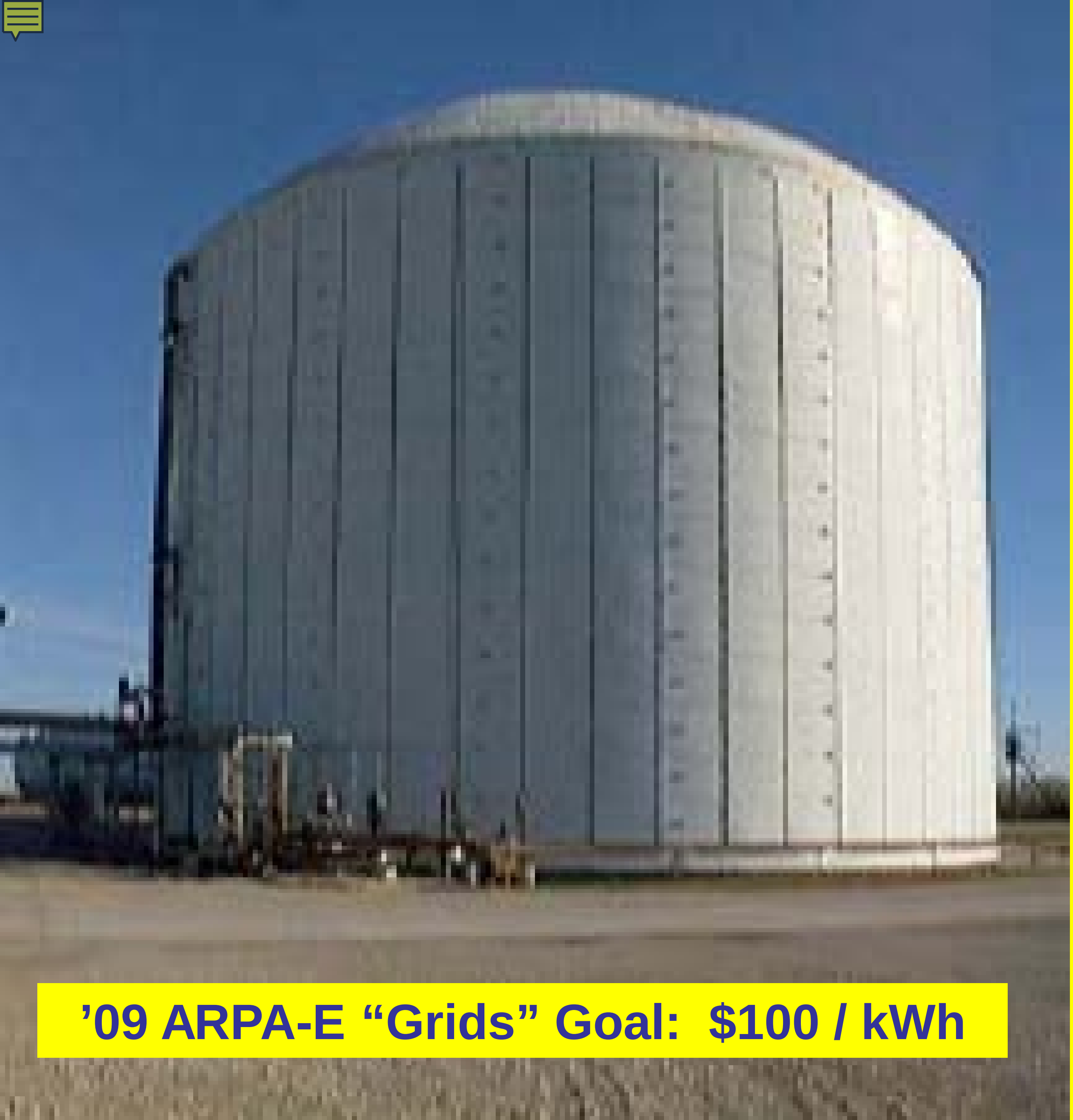

Energy consumption ~12,000 kWh per ton $NH_3$

# RE Ammonia Transmission + Storage Scenario






# Beyond Haber-Bosch "BHB"



'09 ARPA-E "Grids" Goal:  $100 / kWh

*"Atmospheric" Liquid Ammonia Storage Tank (corn belt)*

*30,000 Tons*

*190 GWh*

*$ 15M turnkey*

*$ 80 / MWh*

*$ 0.08 / kWh*

*-33 C*

*1 Atm*

# *NH3 Synthesis Technologies*

– WindToGreen, LLC , 2013

Technology Advisory Group

– Landscape assessment

– Literature search

– Personal followup with researchers

# *NH3 Synthesis Technologies*

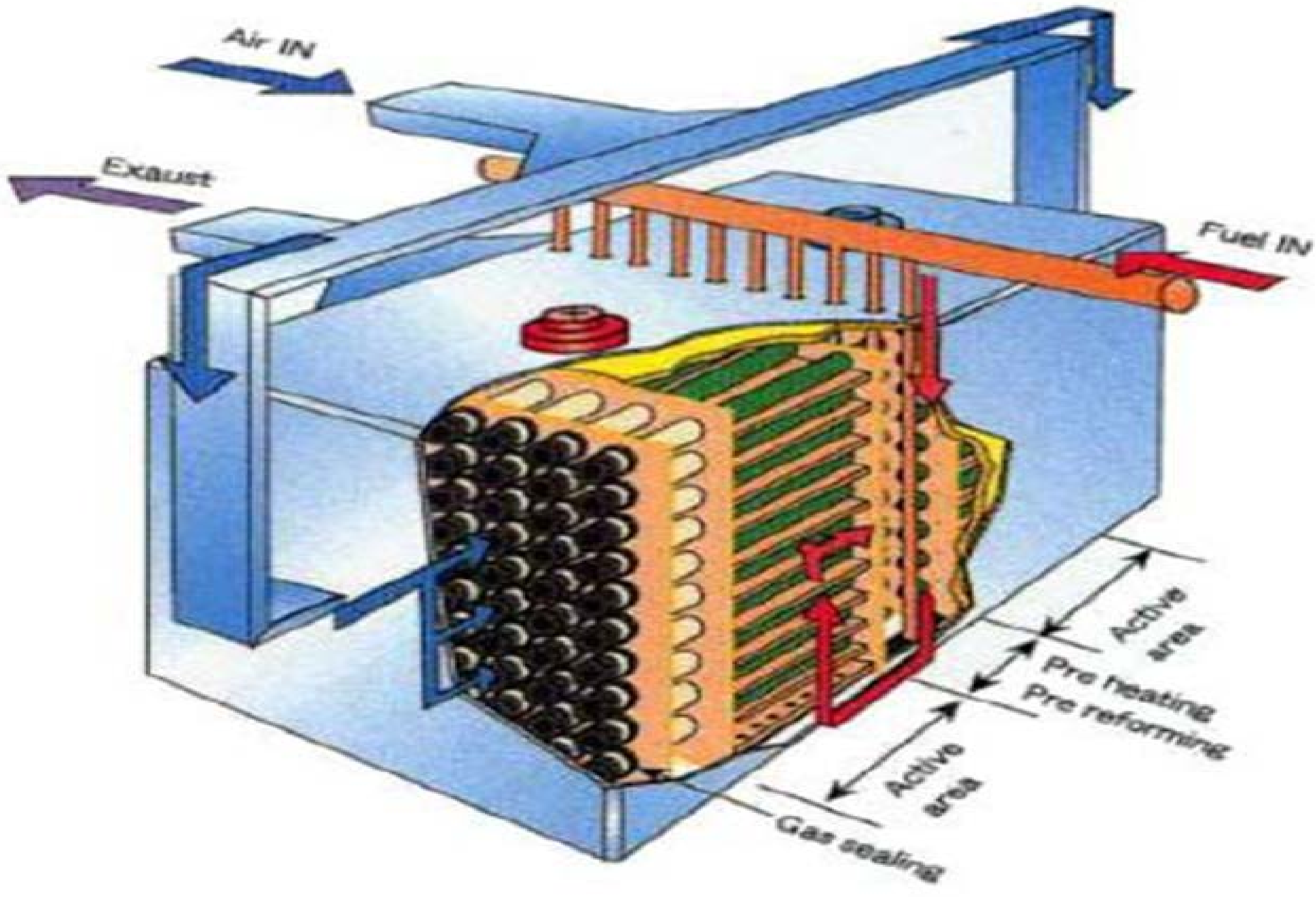
- Haber-Bosch (H-B) and electrolysis plus H-B (EHB)
- Polymer membrane: nano as enabling technology
  - Nanoparticle catalyst impregnated polymer membrane
  - Nanostructure catalyst
  - Nanostructured polymer membrane
  - Other nanoparticles catalysts and nanostructure catalyst carriers
  - Composite electrolytes
- Polymer membrane “Nafion”: not compatible with NH3
- Ammonia-Compatible Polymer (UMinnesota)
  Marc Hillmyer’s Nanostructured PEM,
  alleged to be durable in NH3
- Membrane Electrode Assembly (MEA): PEM fuel cell

# NH3 Synthesis Technologies

- Proton Conducting Ceramic (PCC) electrolytes:
  Examples ($BaCeO_3$, $CaZrO_3$, $SrZrO_3$, $LaGaO_3$)
- Other PCC: $MP_2O_7$ Intermediate-temp PCC + M-N catalysts at Los Alamos National Lab (LANL)
- Oxides:
  - Complex perovskite-type
  - Pyrochlore-type
  - Fluorite-type
- Oxygen ion conducting ceramic electrolyte
- Plasma
  - Non Thermal (NTP)
  - Microwave

# Beyond Haber-Bosch "BHB"

**Emulate SOFC construction**



# *NH3 Synthesis Technologies*

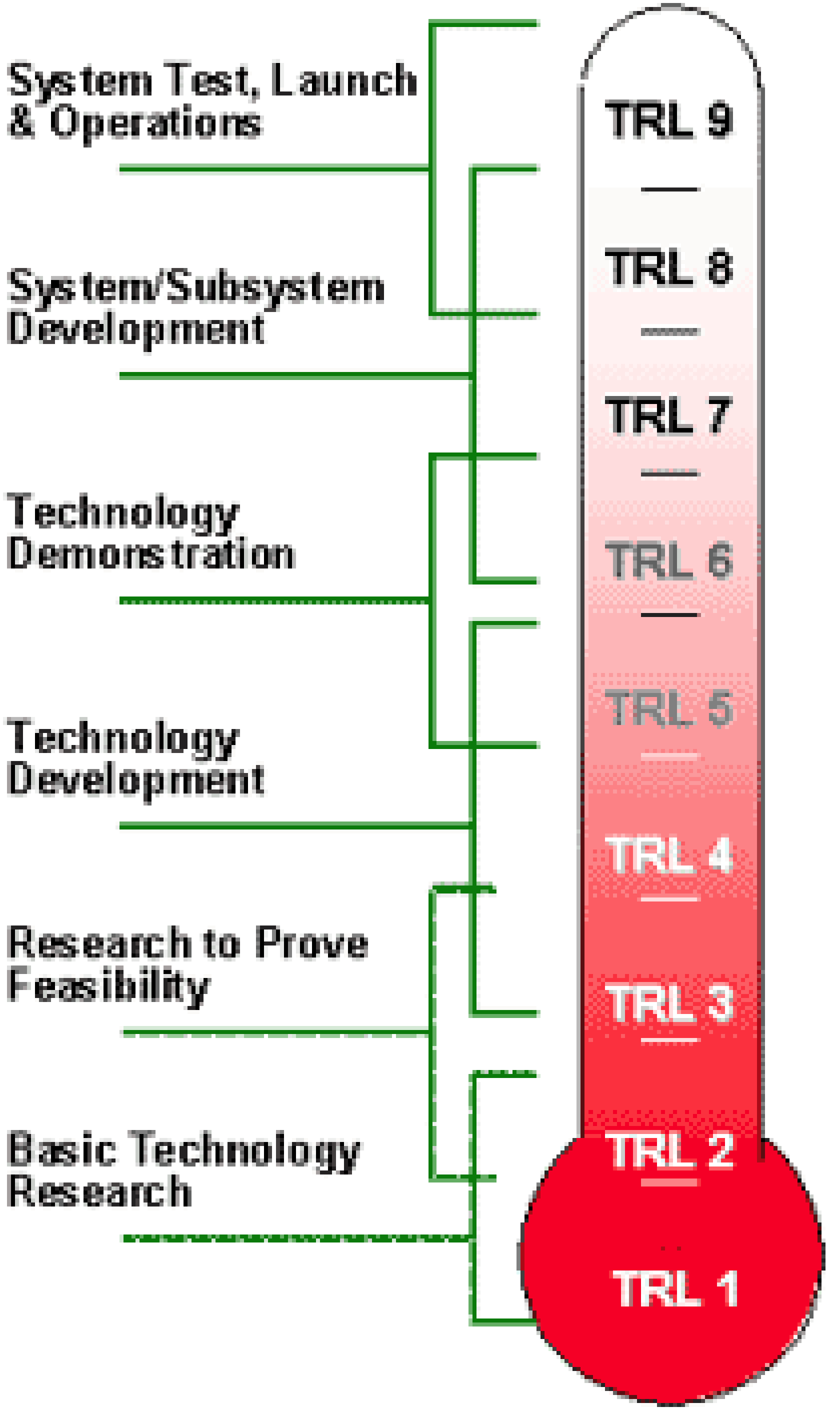
- Molten salt electrolyte
  - Licht
  - Hyung Chool Yoon
- Ionic Liquid electrolyte
- Diamond nanoparticles catalyst, substrate, deep UV light: U. Wisconsin Madison (R.J. Hamers)
- Solar-assisted two-stage metal nitride redox, low-P NH3 synth, from ETH, Zurich
- N2 Cleavage and Hydrogenation by a Trinuclear Titanium Polyhydride Complex
- Cyclic Pressurization (ICE)
- Lithium (proprietary)

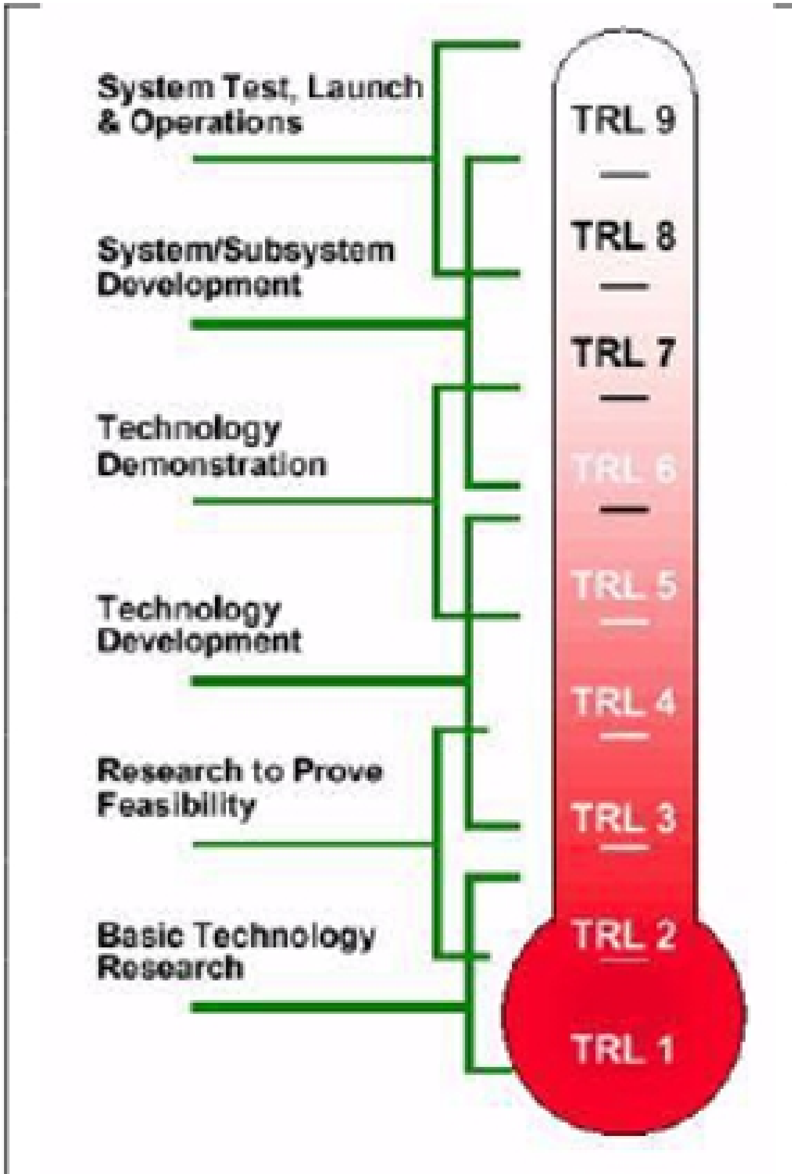
# *H2 generation to feed H-B*

– Artificial Photosynthesis (AP)
– Catalyst pseudo-random search: JCAP
– Biology: algae, other
– Gasification
– Nanoptek, proprietary:

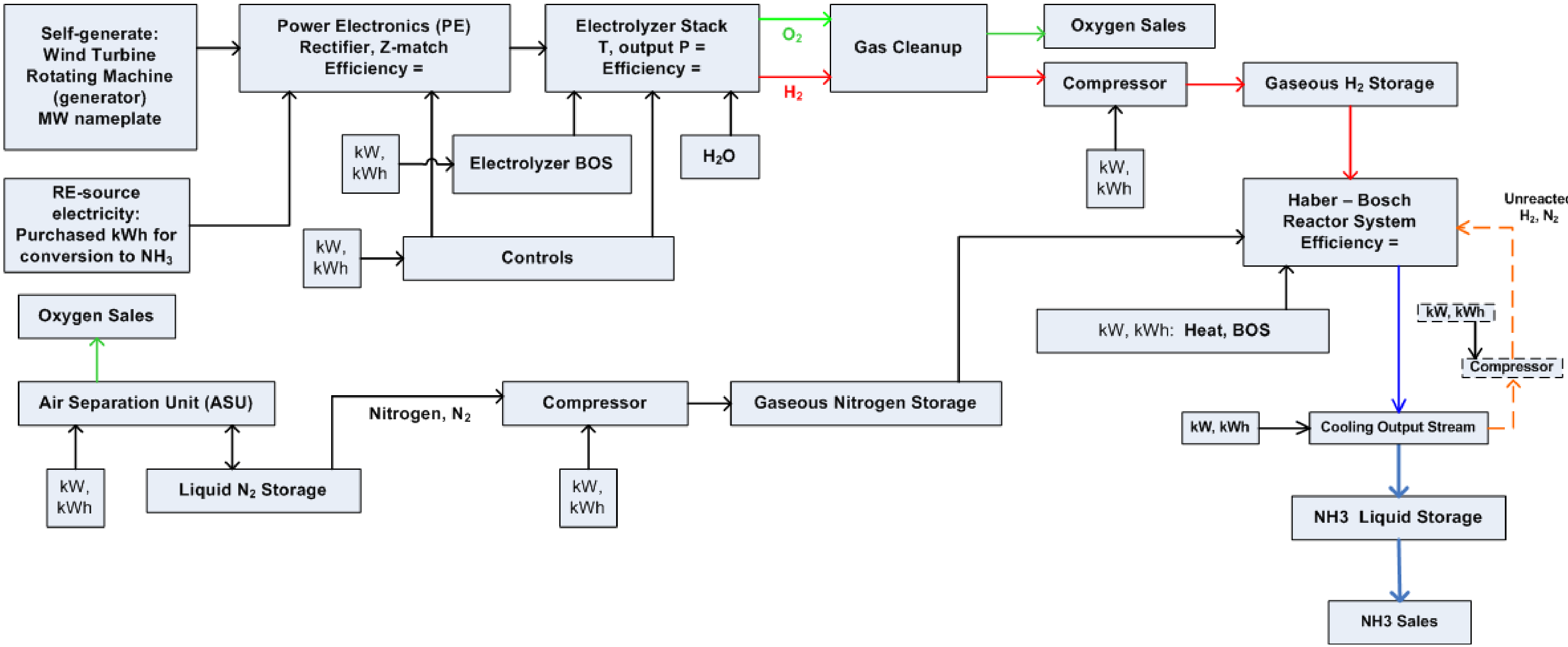
light or electricity input → H2

– Other


System Test, Launch & Operations
System/Subsystem Development
Technology Demonstration
Technology Development
Research to Prove Feasibility
Basic Technology Research
TRL 9
TRL 8
TRL 7
TRL 6
TRL 5
TRL 4
TRL 3
TRL 2
TRL 1




| |
|---|
| Actual Technology qualified through successful mission operations |
| Actual Technology completed and qualified through test and demonstration |
| Technology prototype demonstration in a simulated operational environment |
| Prototype demonstration in a relevant environment |
| Technology basic validation in a relevant environme |
| Technology basic validation in a laboratory environment |
| Analytical and experimental critical function and/or characteristic proof of concept |
| Technology concept and/or application formulated |
| Basic principles observed and reported |




# Electrolysis + Haber-Bosch (EHB) system
# For RE-source Electricity, Water, and Air inputs

# Review of electrochemical ammonia production technologies and materials

S. Giddey, S.P.S. Badwal, A. Kulkarni

CSIRO Energy Technology
Victoria, Australia

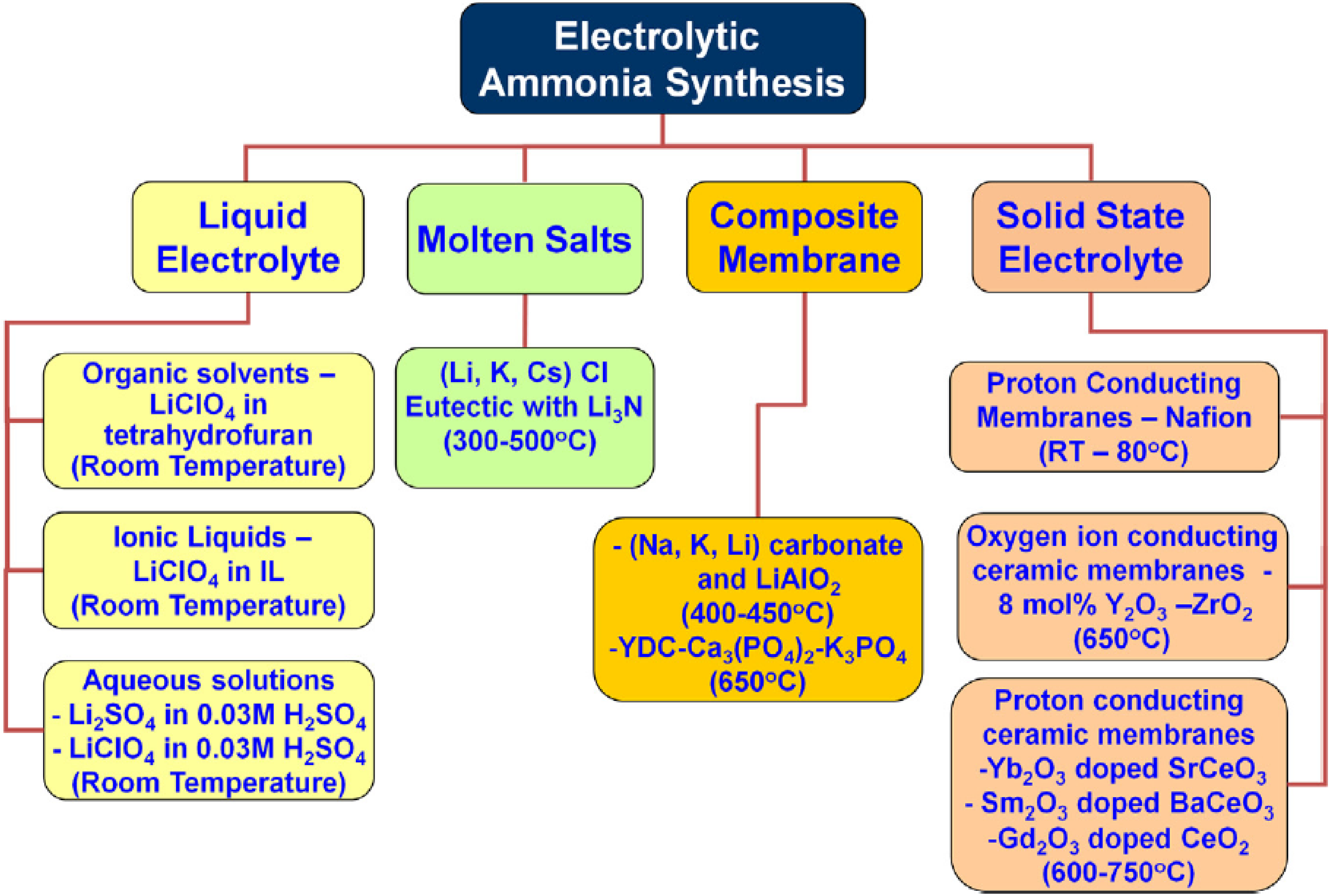
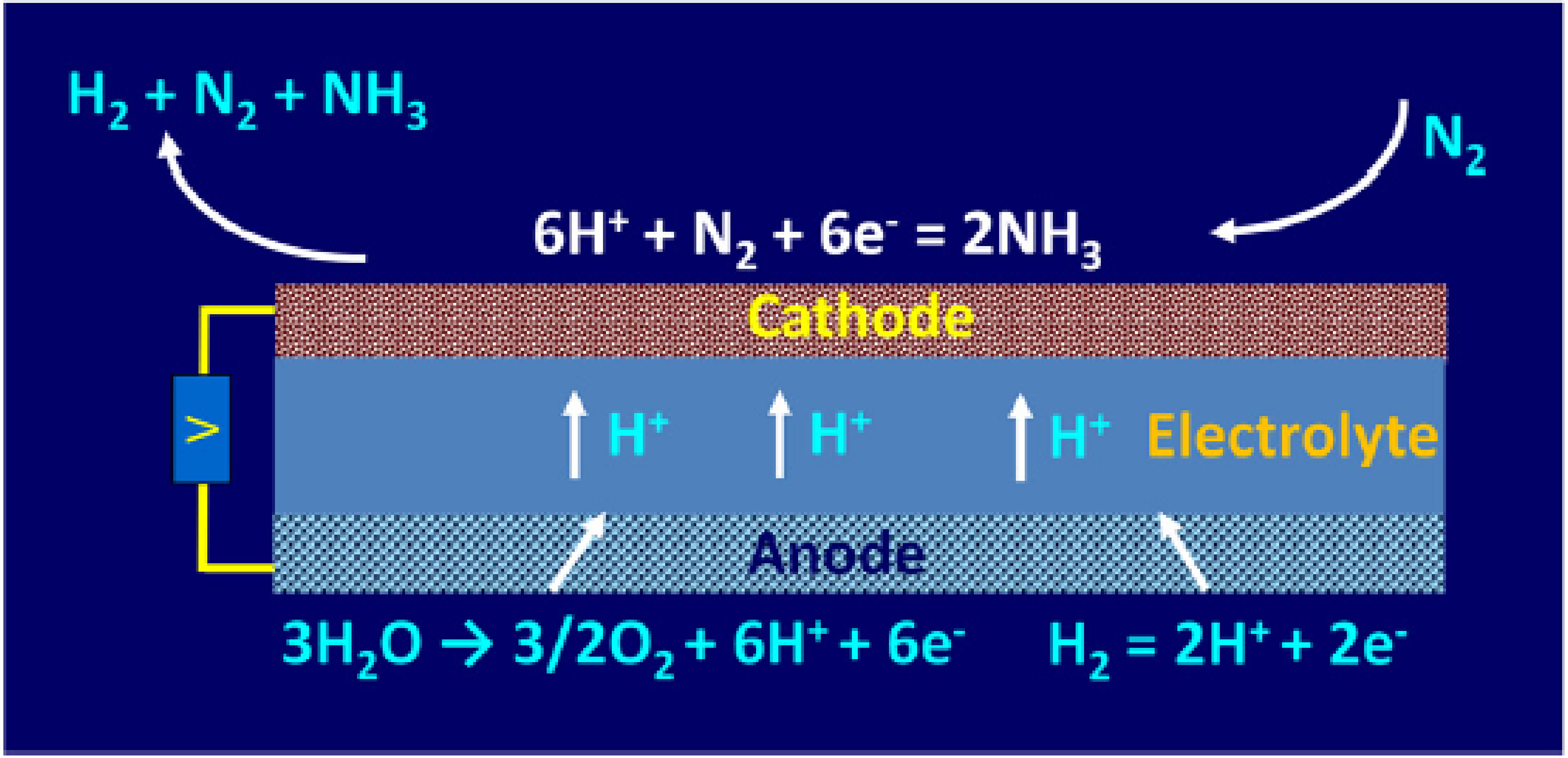
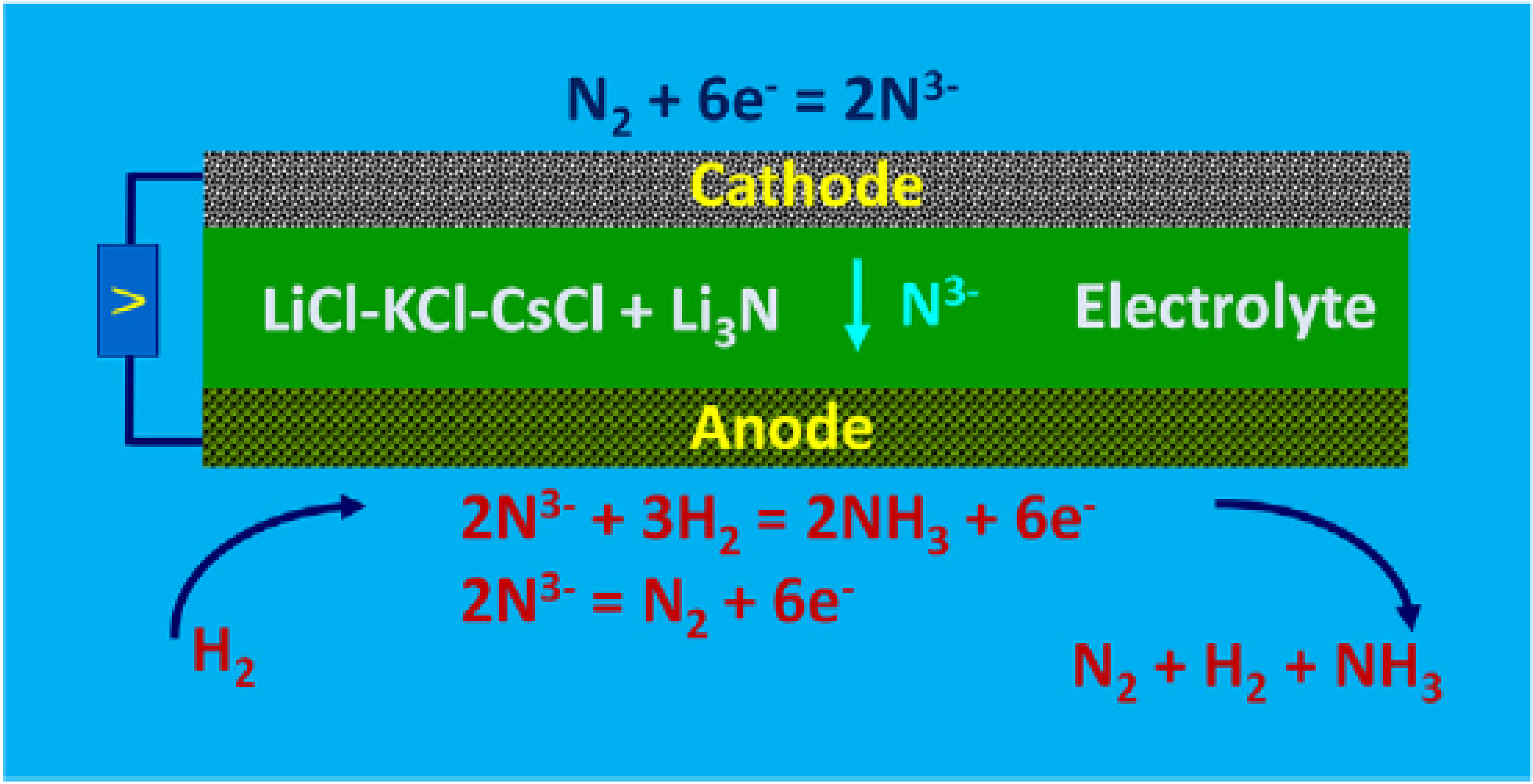


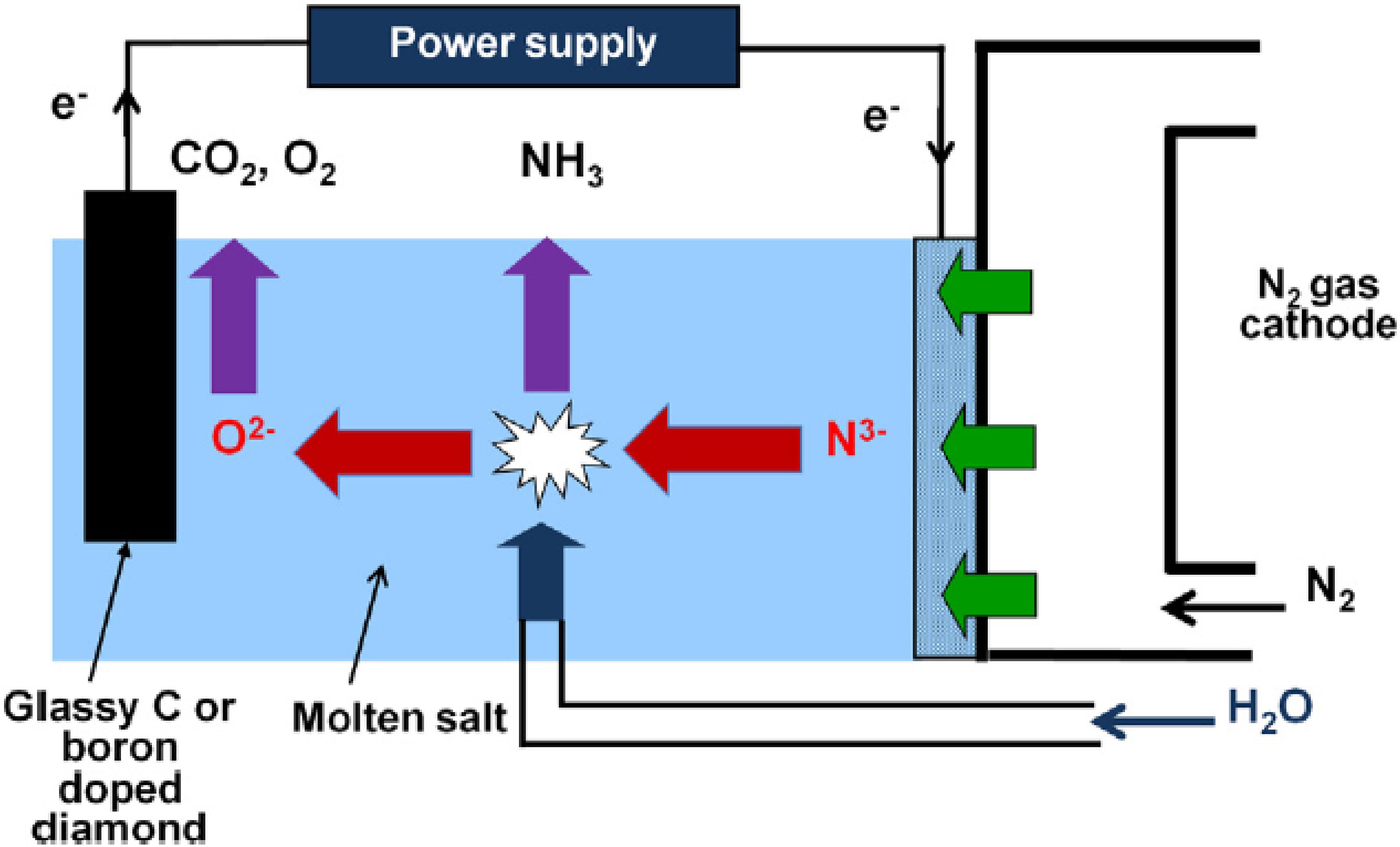

Fig. 2 — Various electrolytic options under consideration for ammonia synthesis.



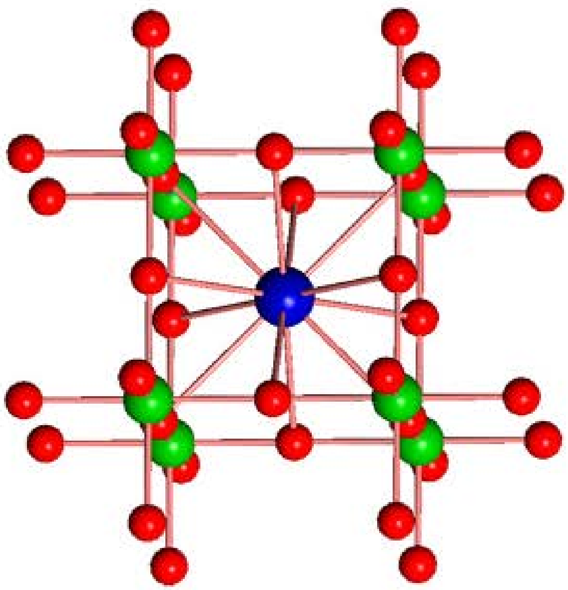

# NH3 Synthesis by Proton Conducting Solid Electrolyte

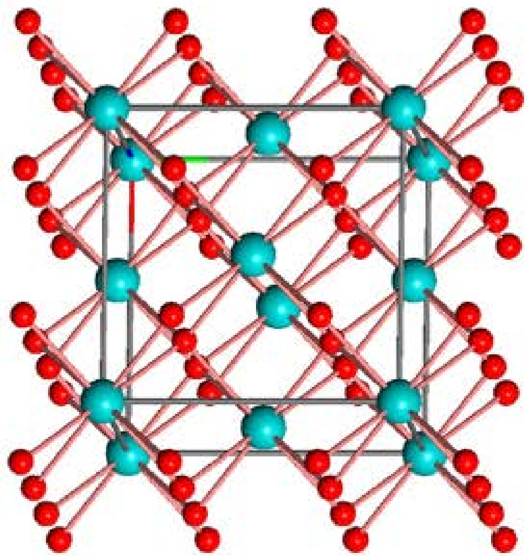


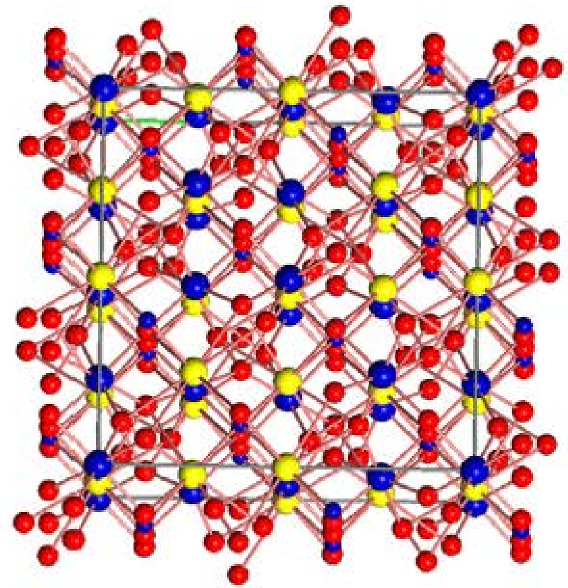

# NH3 Synthesis by Molten Salt Electrolyte



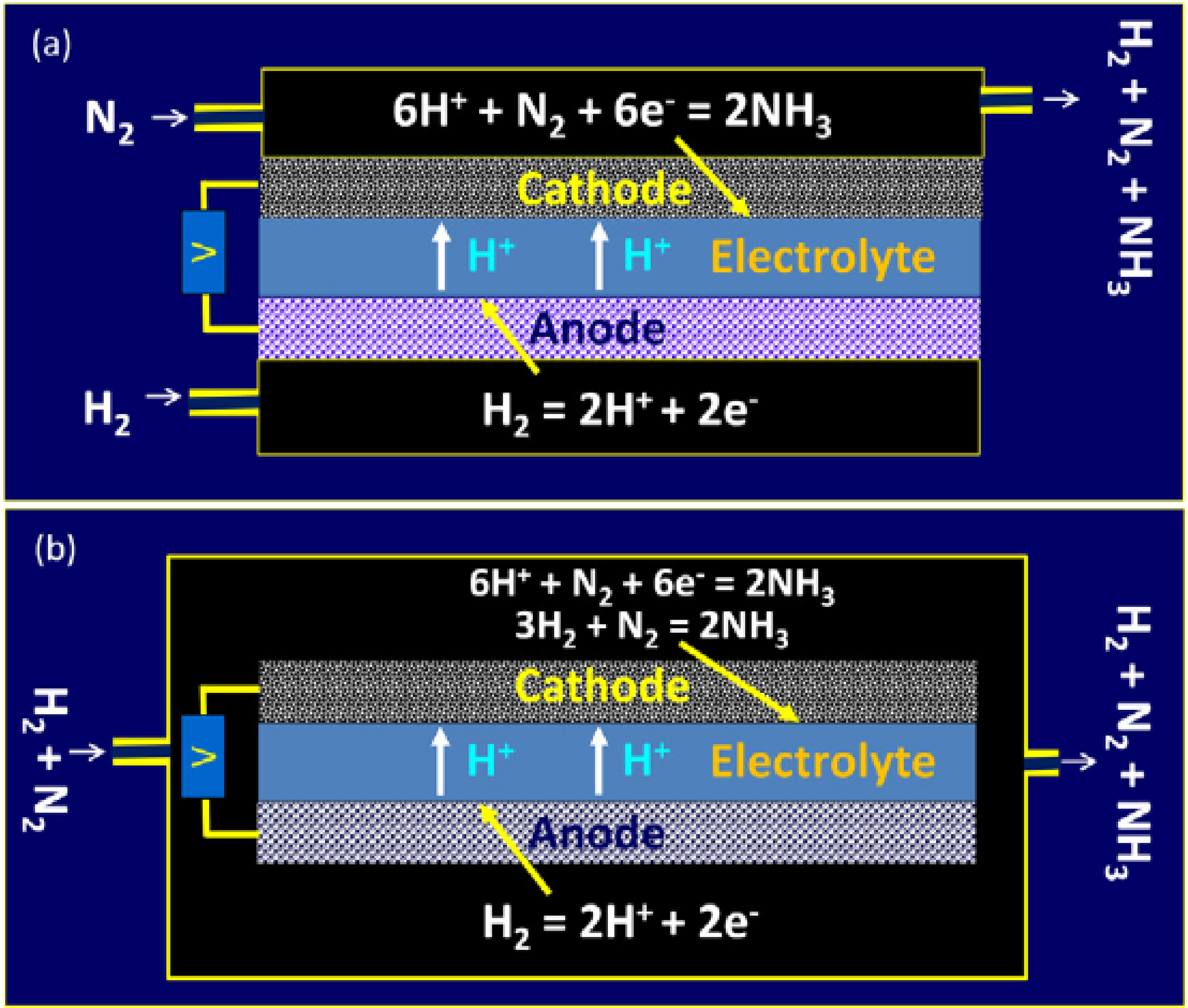

**NH3 Synthesis via Molten Salt Electrolyte With Water as Hydrogen Source**





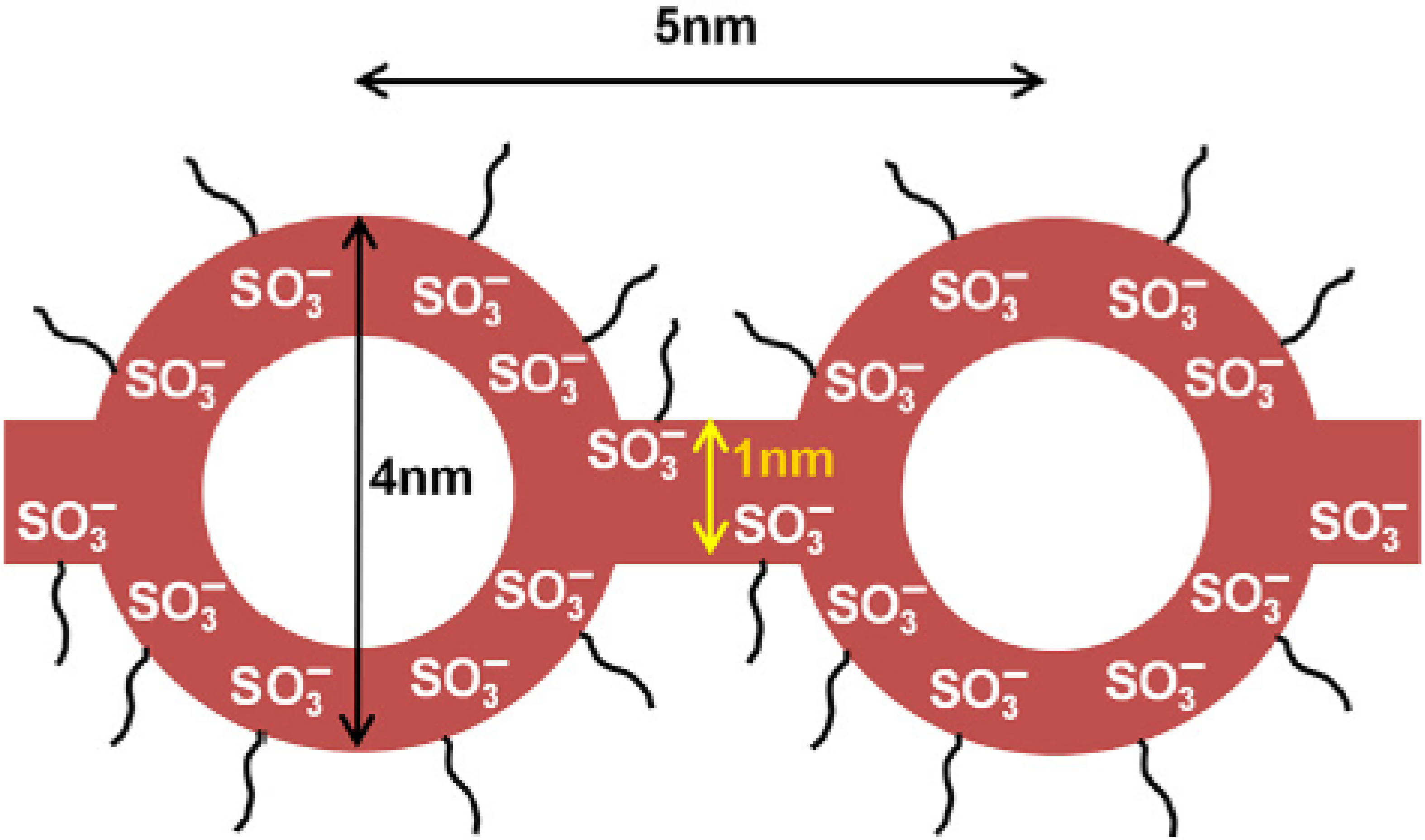


**Perovskites** **Fluorites** **Pyrochlores**




**Proton Conducting Ceramic Electrolyte Cell**

**TOP: Double-chamber** **BOTTOM: Single-chamber**

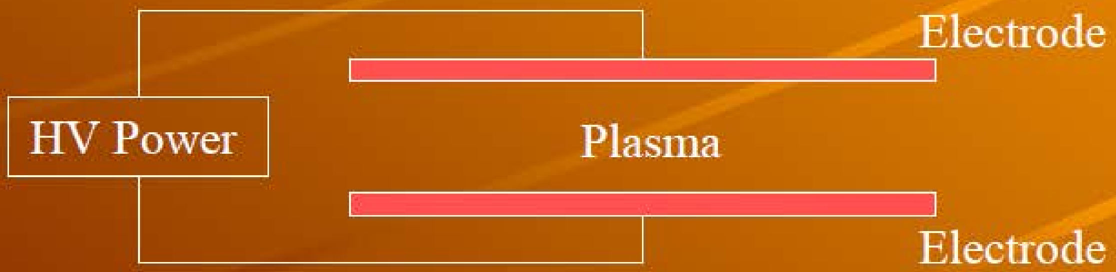



**Cluster Model of "NAFION" Membrane**
**~ $10^{-8}$ mol per $cm^2$ per second**

# What is NTP?

- NTP species include: energetic electrons, photons, atoms, and molecules, highly reactive radicals, ozone, etc. Ozone is the most widely used NTP species.
- NTP is generated though electrical discharge in gas (in atmosphere or liquid).

**Highest single-pass conversion = 13%**

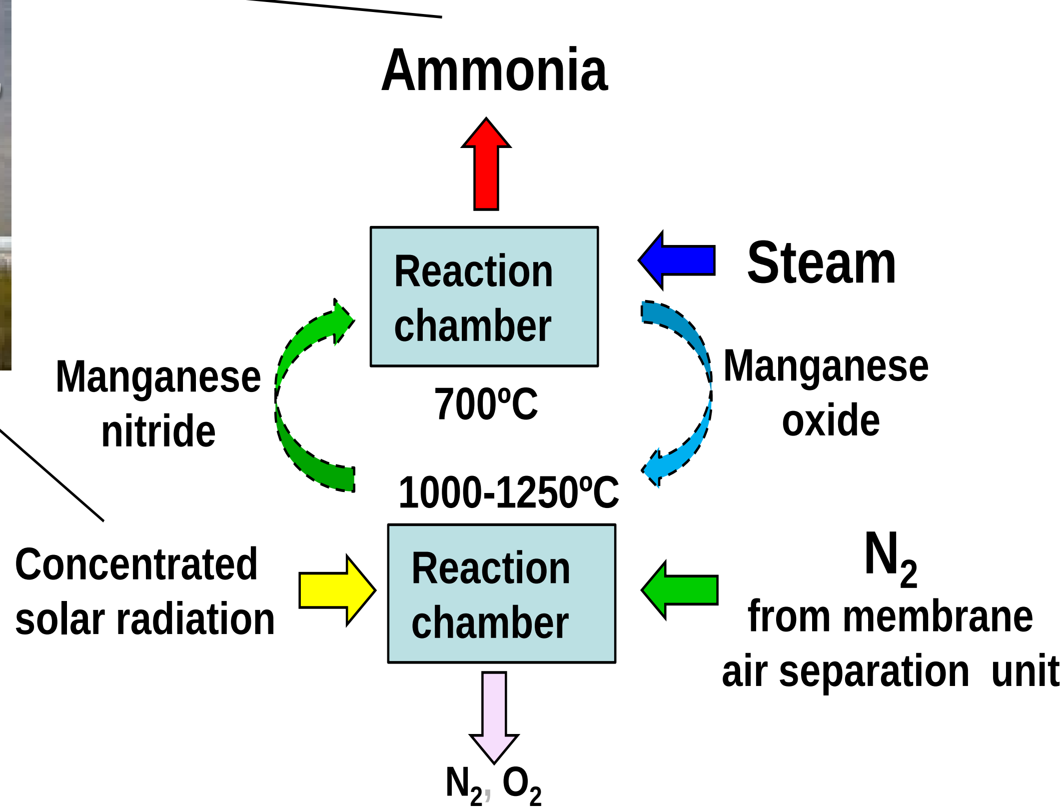



**Source: Roger Ruan, University of Minnesota**

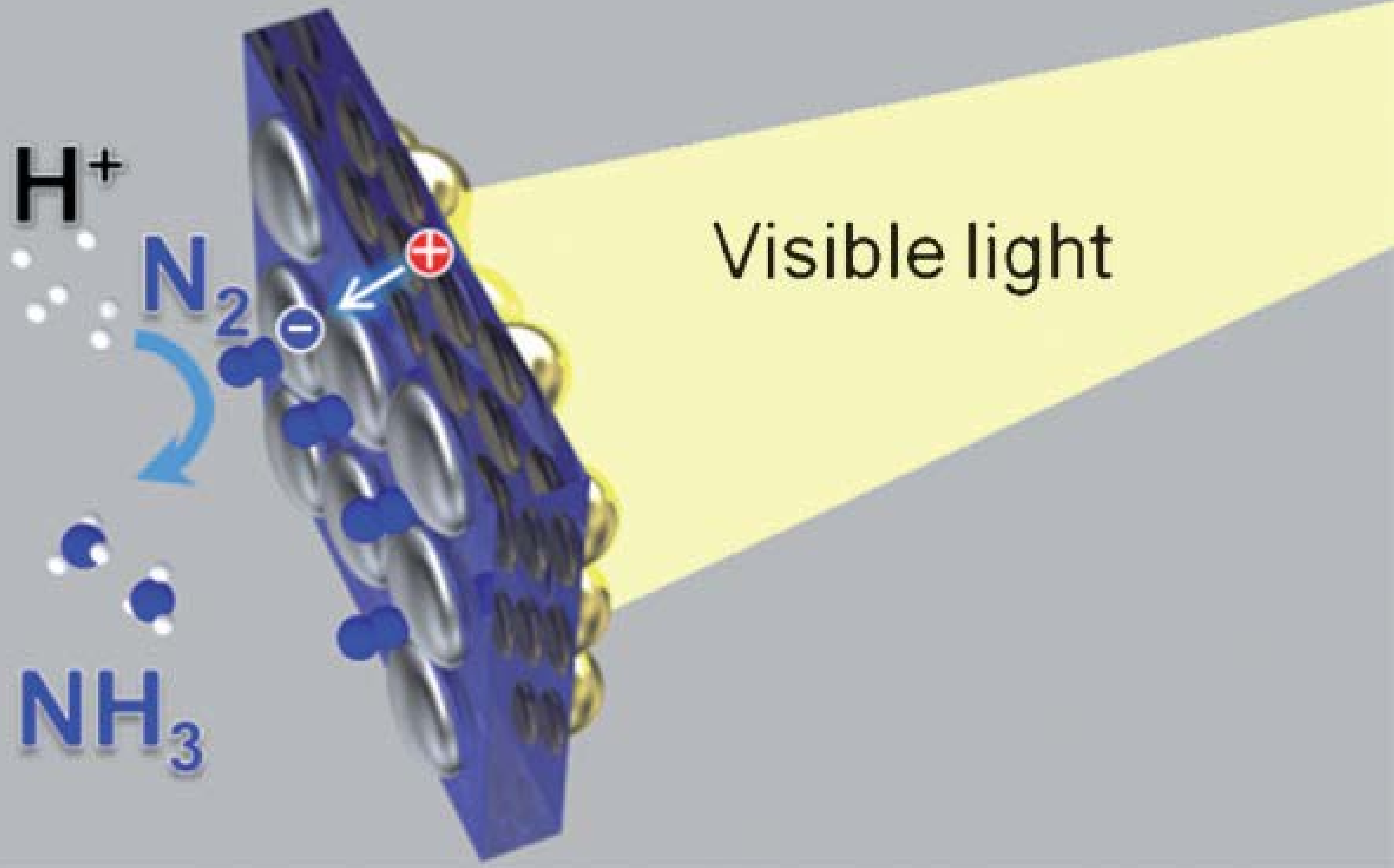
# Solar Thermochemical Ammonia

P. Pfromm, R. Michalsky*, Kansas State University

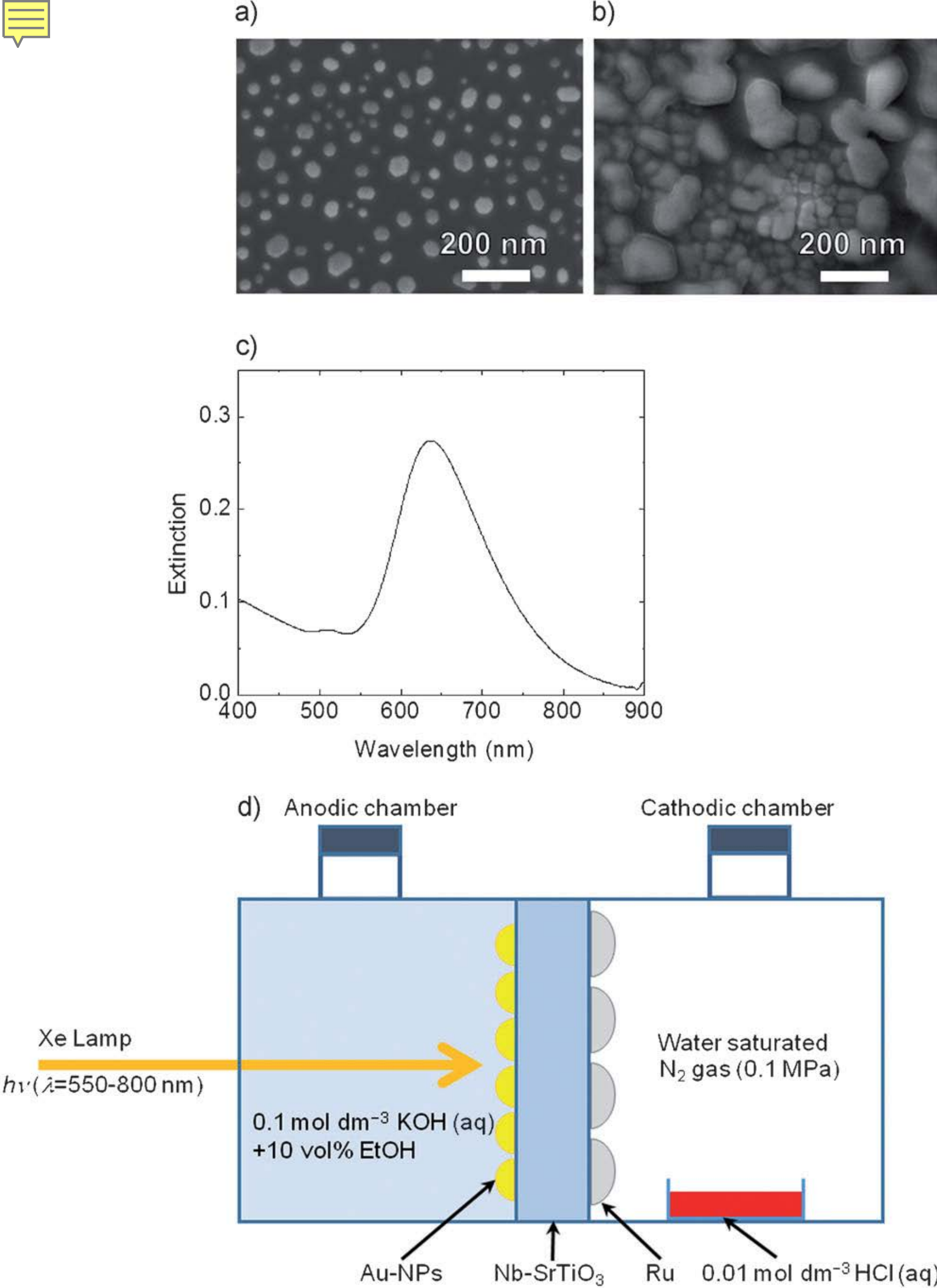

Solar tower with heliostats

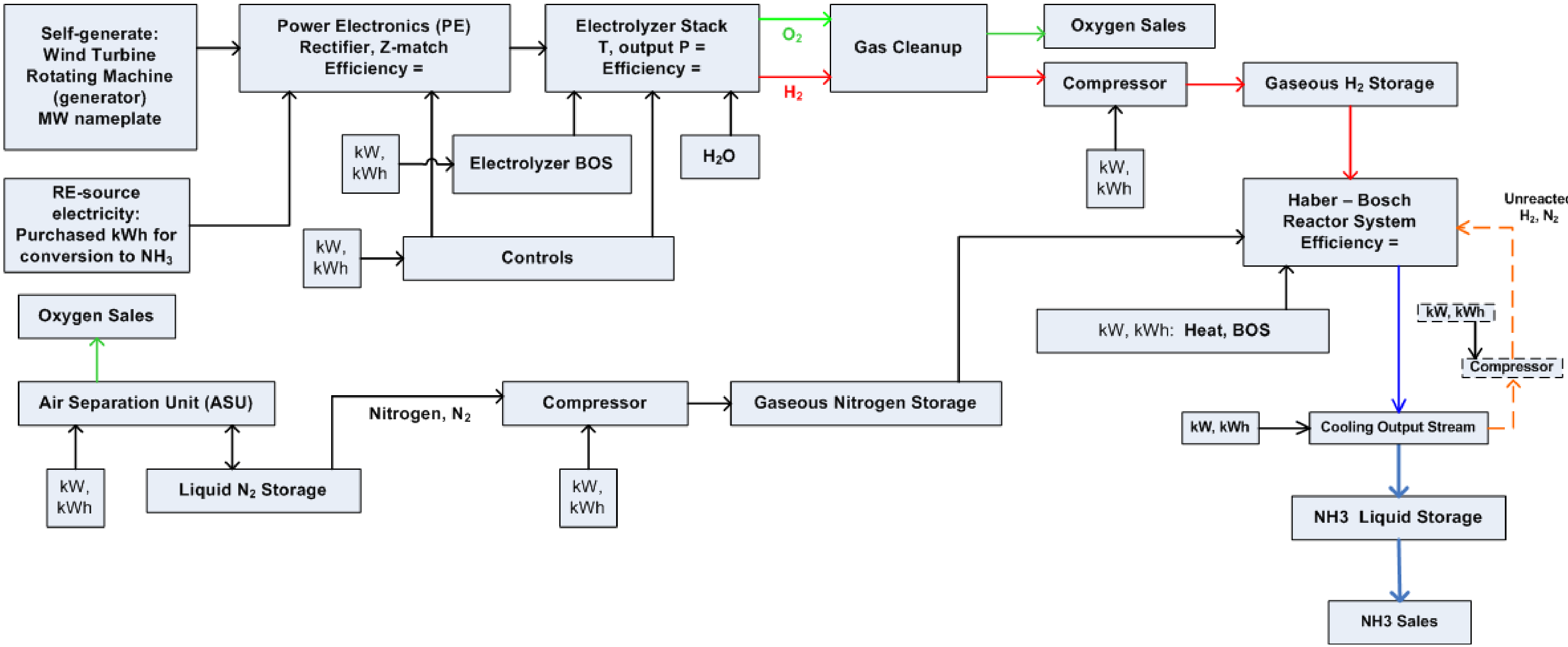



*now ETH, Zurich

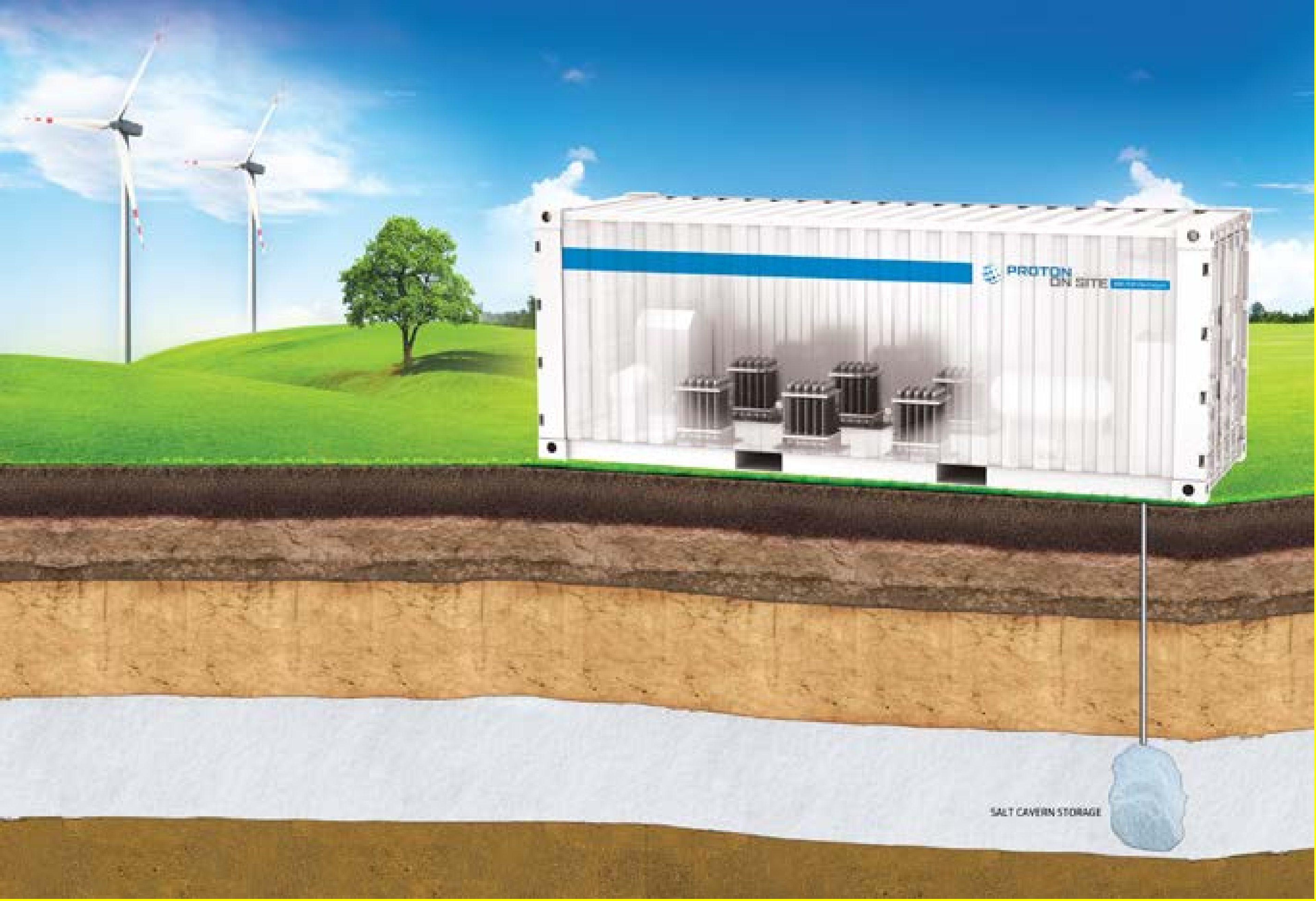



**Plasmon-Induced Ammonia Synthesis through Nitrogen Photofixation with Visible Light Irradiation**


a)
200 nm
b)
200 nm
c)
Extinction
0.0
0.1
0.2
0.3
400
500
600
700
800
900
Wavelength (nm)
d)
Anodic chamber
Cathodic chamber
Xe Lamp
hν(λ=550-800 nm)
0.1 mol dm-3 KOH (aq)
+10 vol% EtOH
Water saturated
N2 gas (0.1 MPa)
Au-NPs
Nb-SrTiO3
Ru
0.01 mol dm-3 HCl (aq)



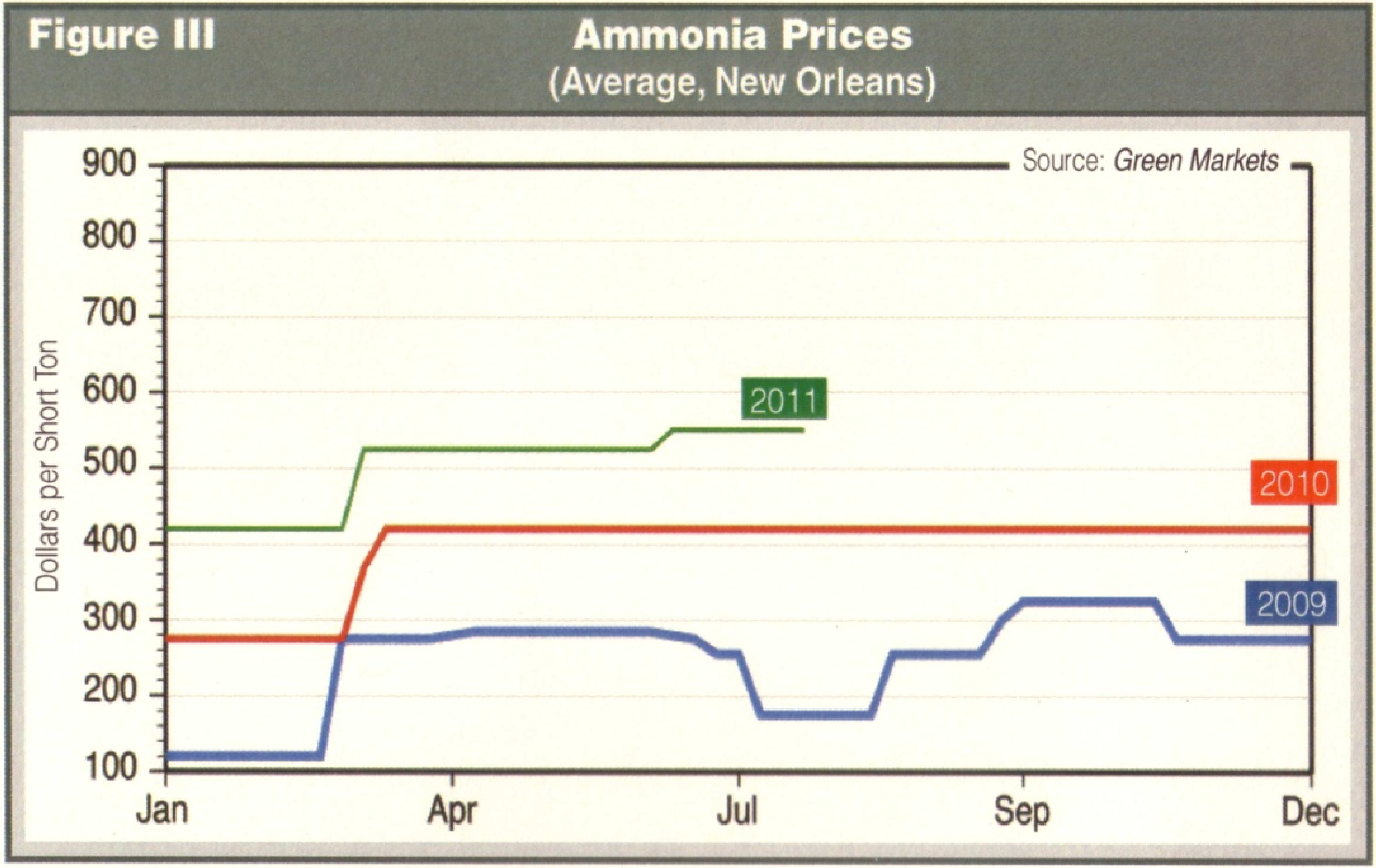

# Ag Ventures Alliance, Mason City, Iowa
# Electrolysis + Haber-Bosch (EHB) system
# For RE-source Electricity, Water, and Air inputs



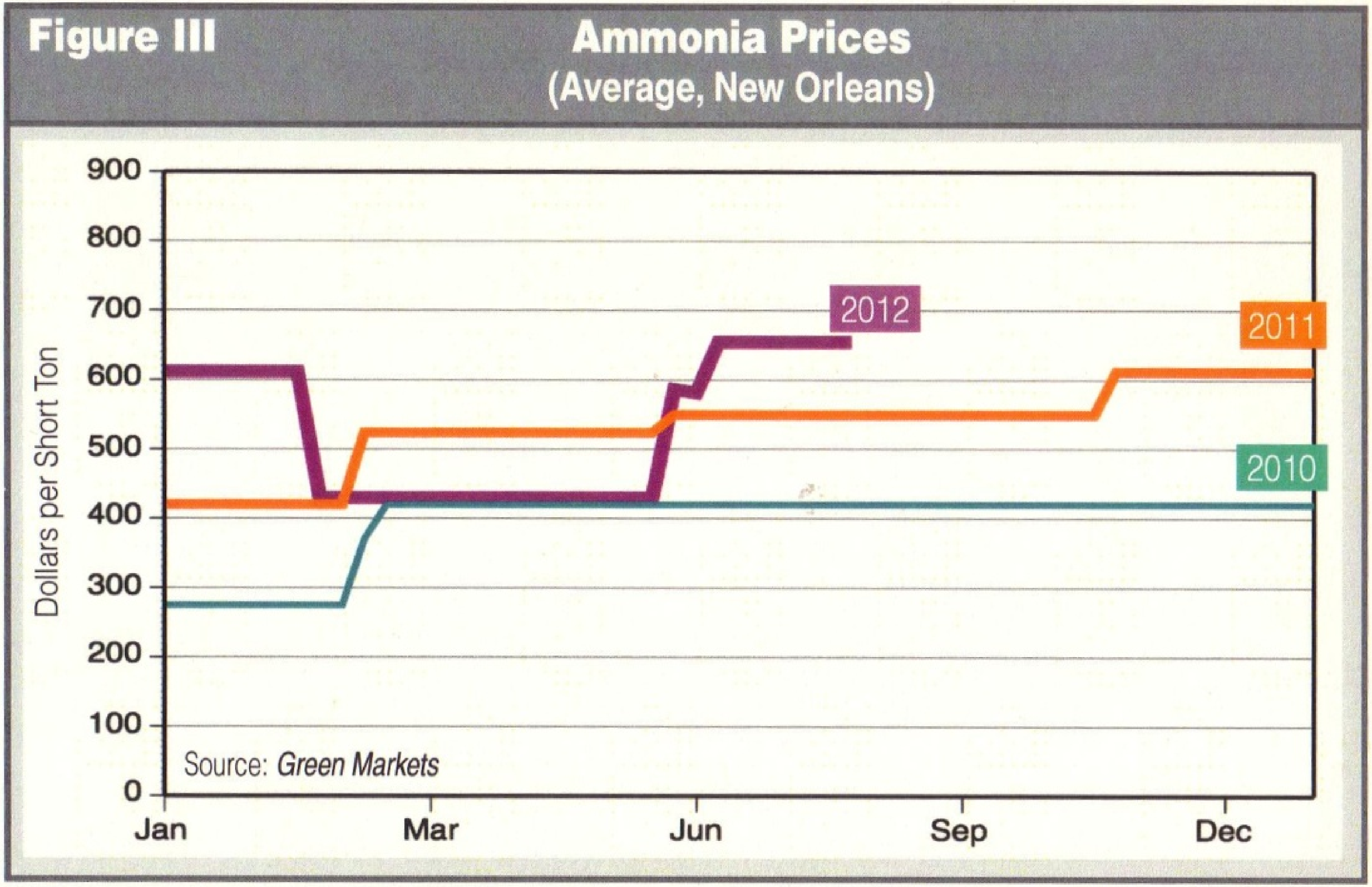

**Source: Proton Onsite**


**Proton Ventures BV, Netherlands**

**www.protonventures.com**




**Source: FINDS, Keith Stokes**

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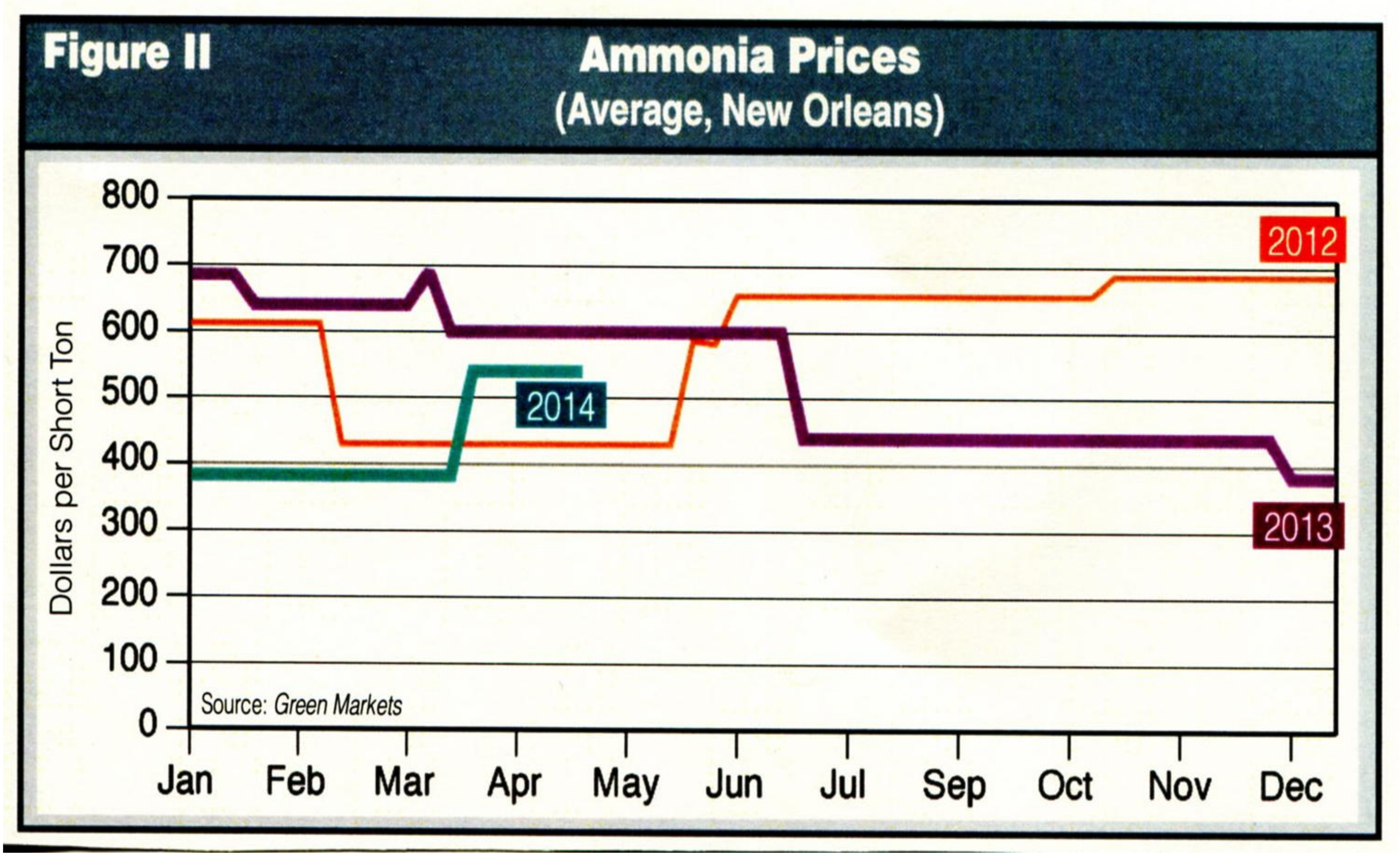
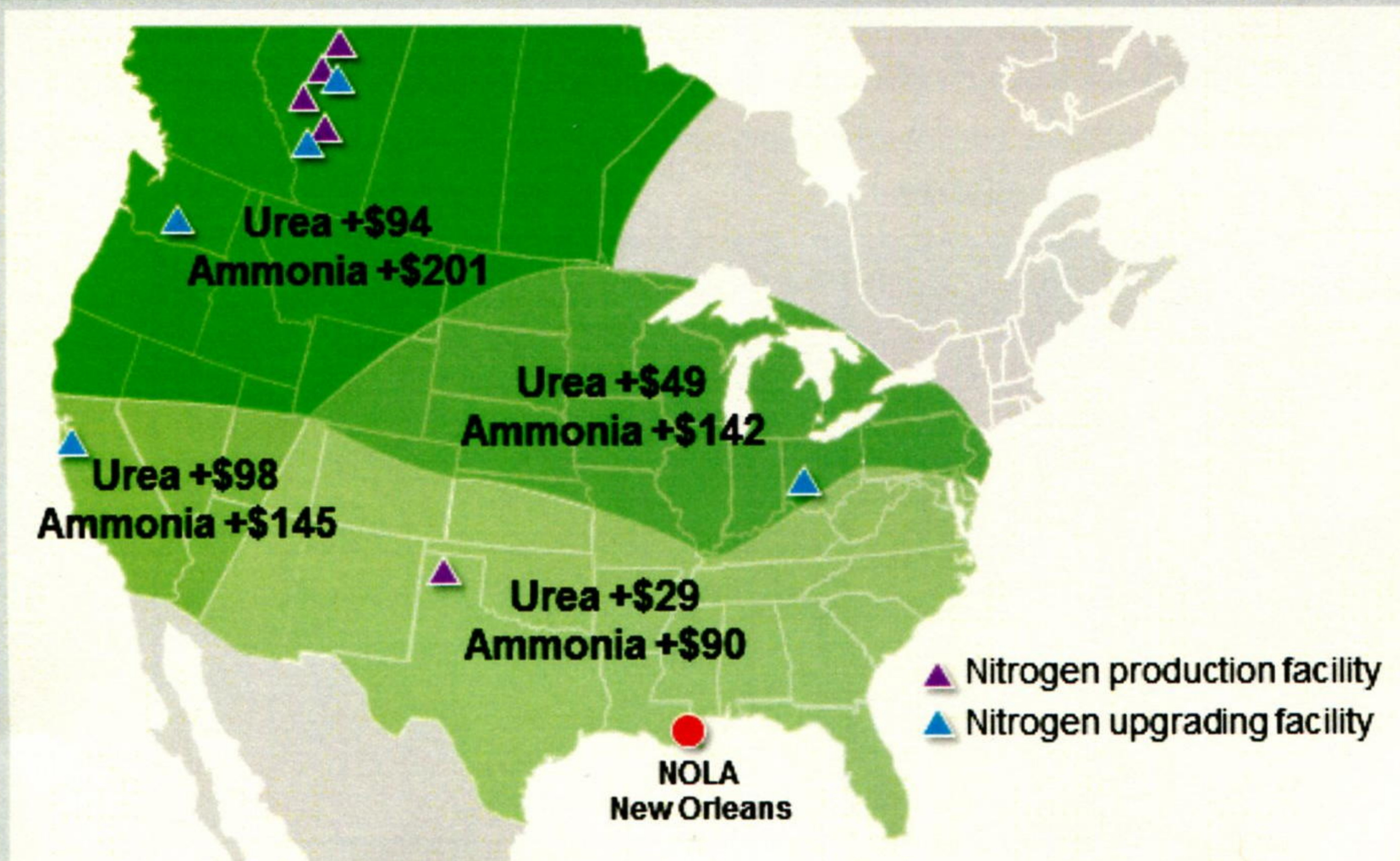



**Source: FINDS, Keith Stokes**

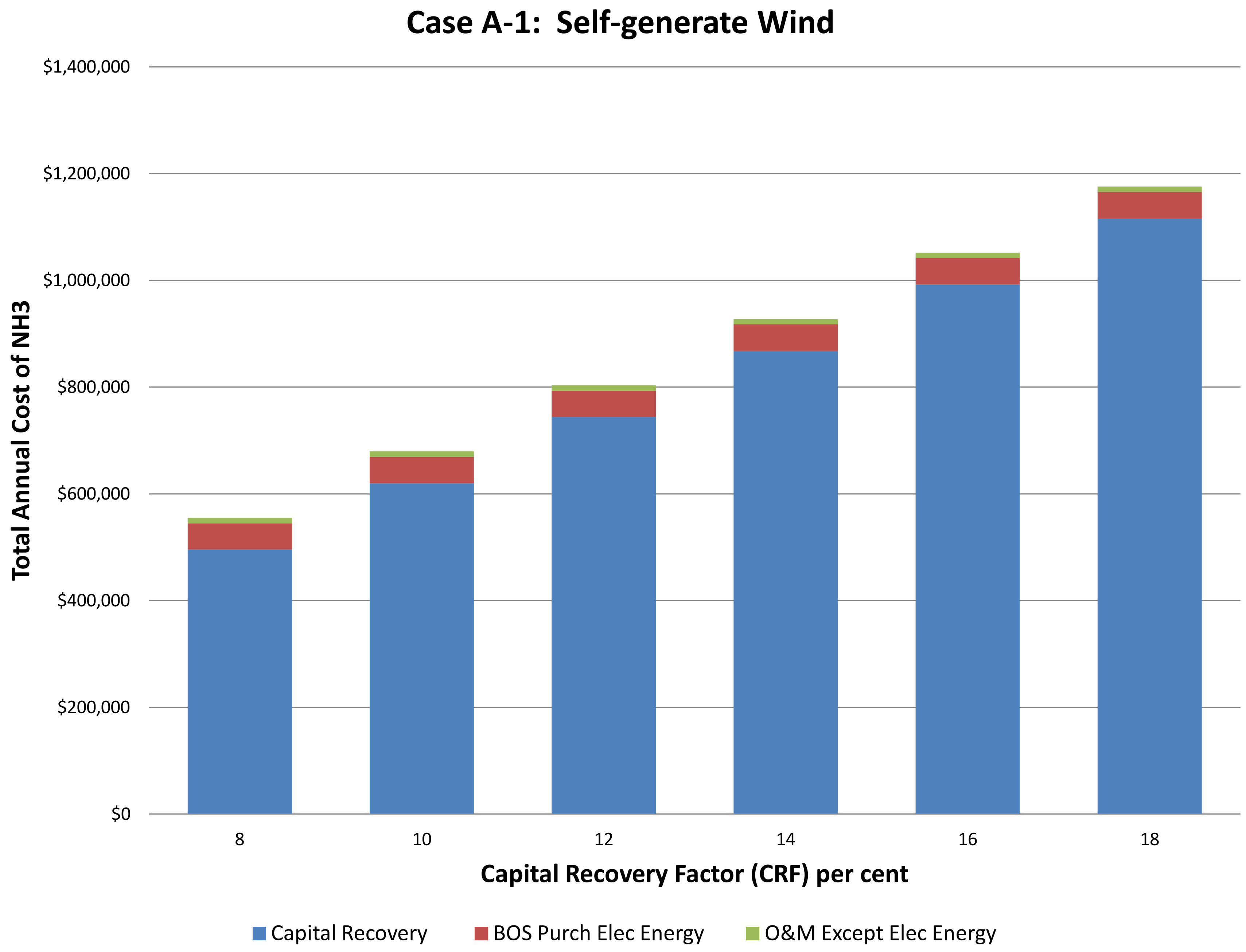
**Figure V** Regional Nitrogen Price Premium Over U.S. Gulf (NOLA) Price ($U.S./metric tonne)

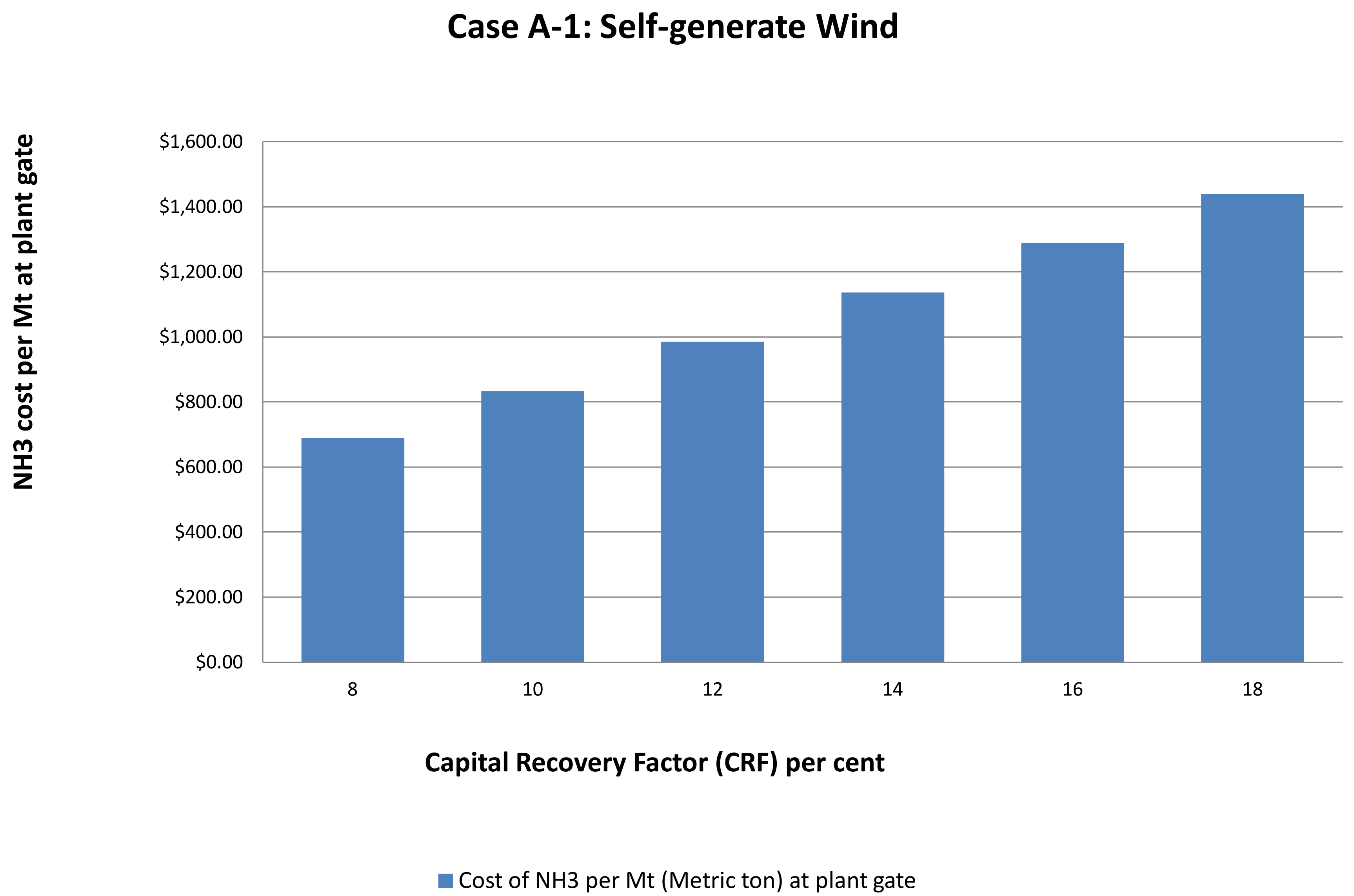


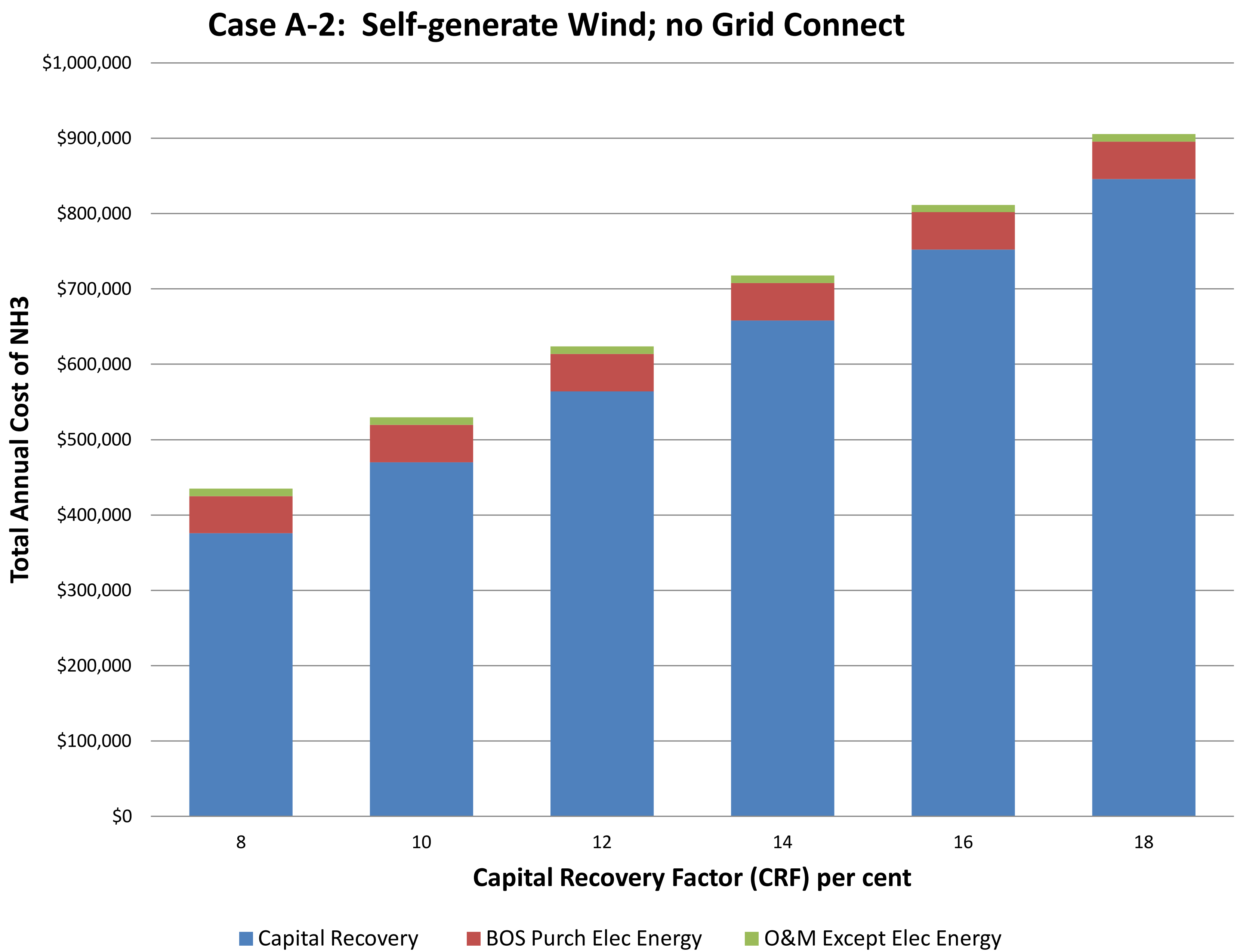

NOTE: Delivered prices adjusted by -$5/t for urea and -$9/t for ammonia to estimate FOB prices. Based on a 10-year average from 2003-2012.

SOURCE: *GreenMarkets*: Spread equals average regional reference price minus NOLA reference price.

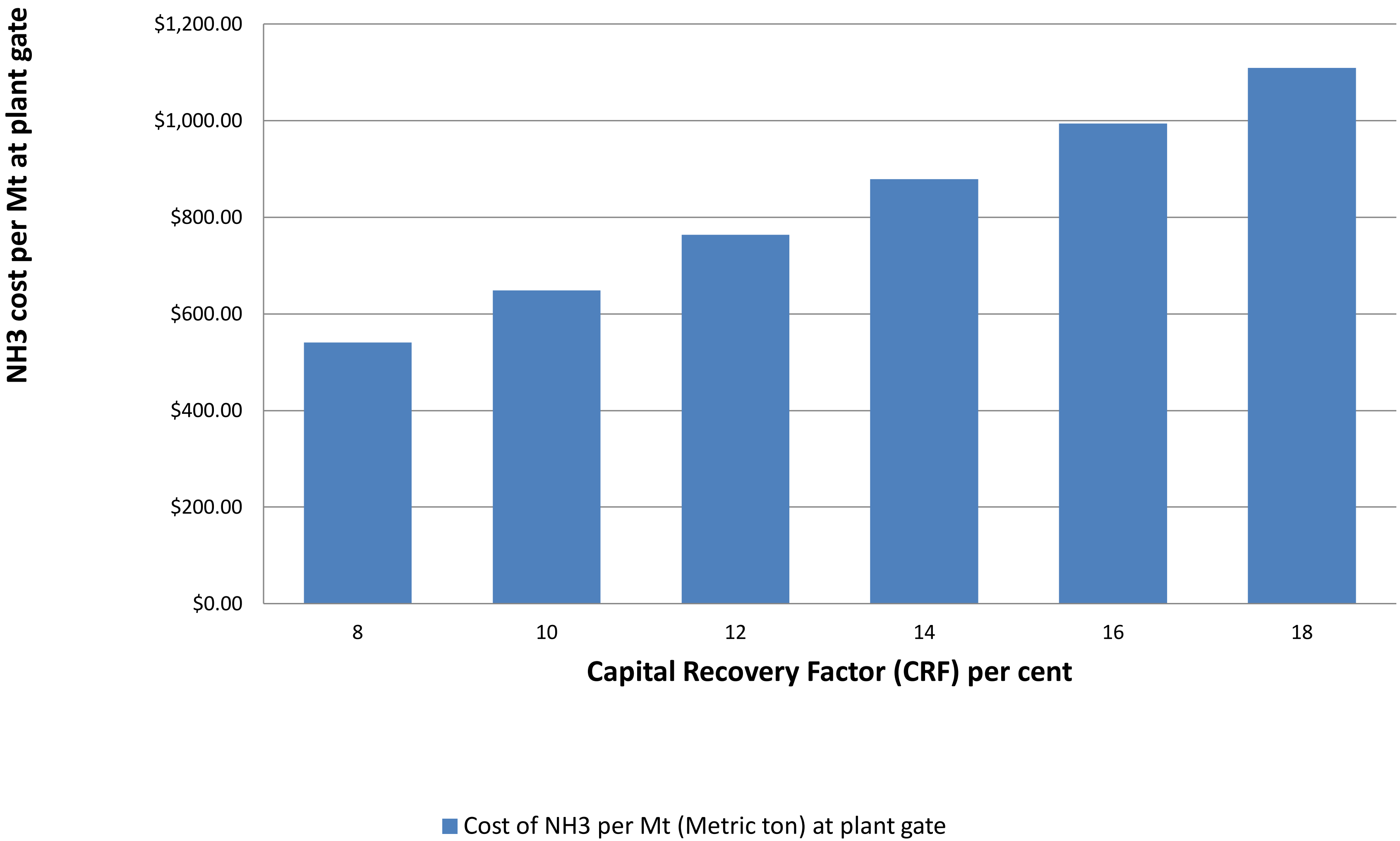
**Source: FINDS, Keith Stokes**

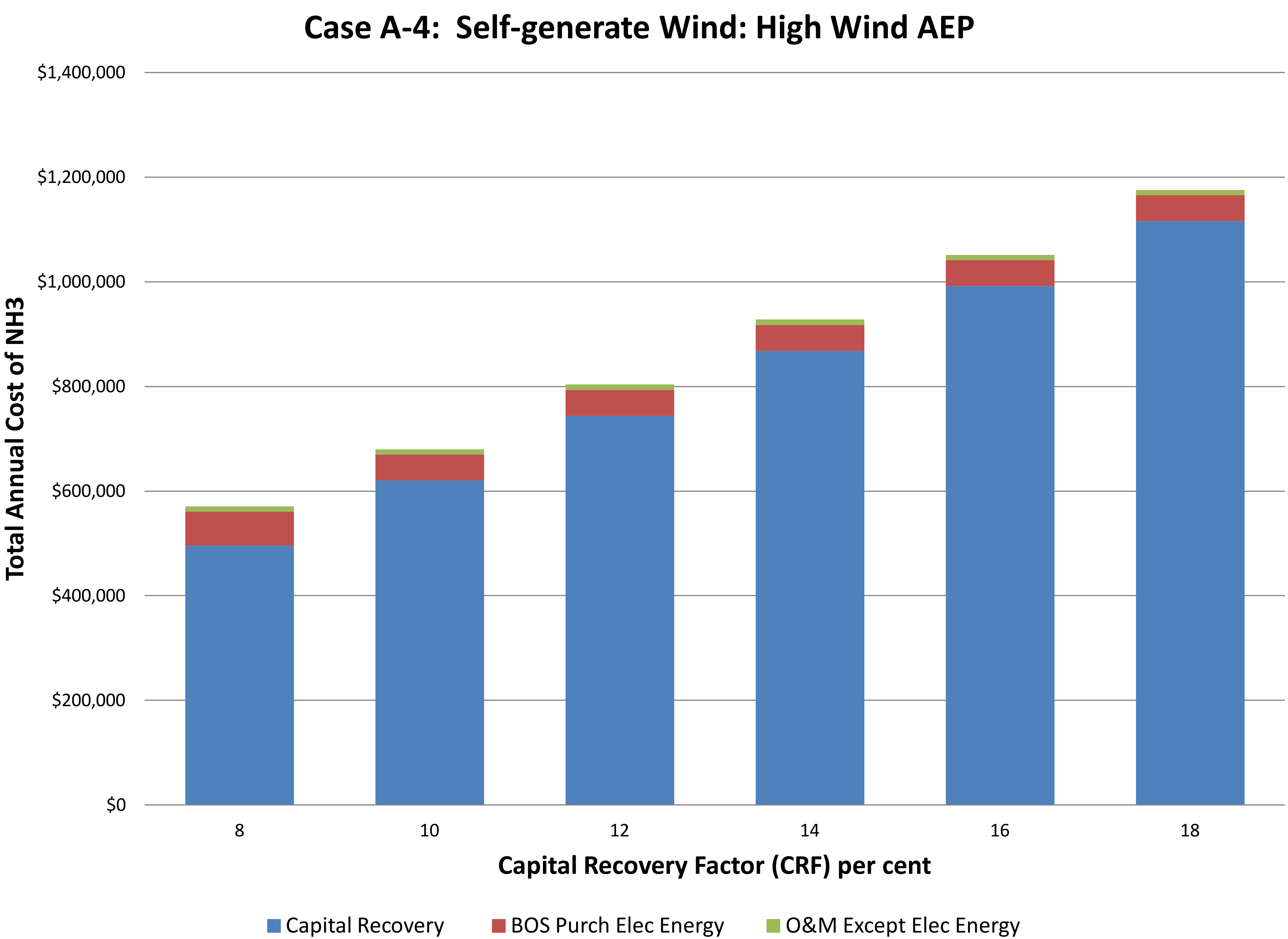

Case A-1: Self-generate Wind
$1,400,000
$1,200,000
$1,000,000
$800,000
$600,000
$400,000
$200,000
$0
Total Annual Cost of NH3
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Capital Recovery
BOS Purch Elec Energy
O&M Except Elec Energy

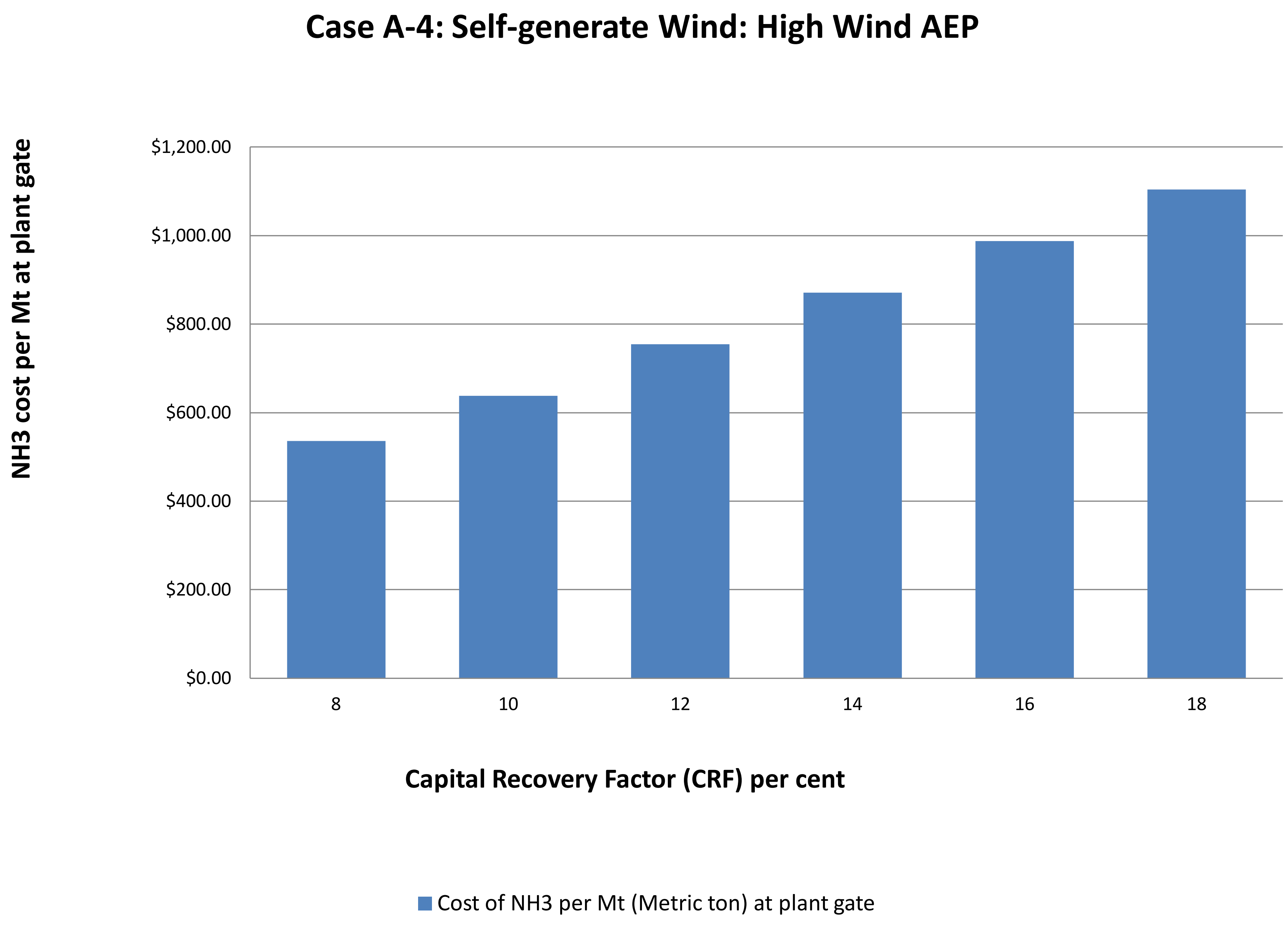

Case A-1: Self-generate Wind
NH3 cost per Mt at plant gate
$1,600.00
$1,400.00
$1,200.00
$1,000.00
$800.00
$600.00
$400.00
$200.00
$0.00
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Cost of NH3 per Mt (Metric ton) at plant gate

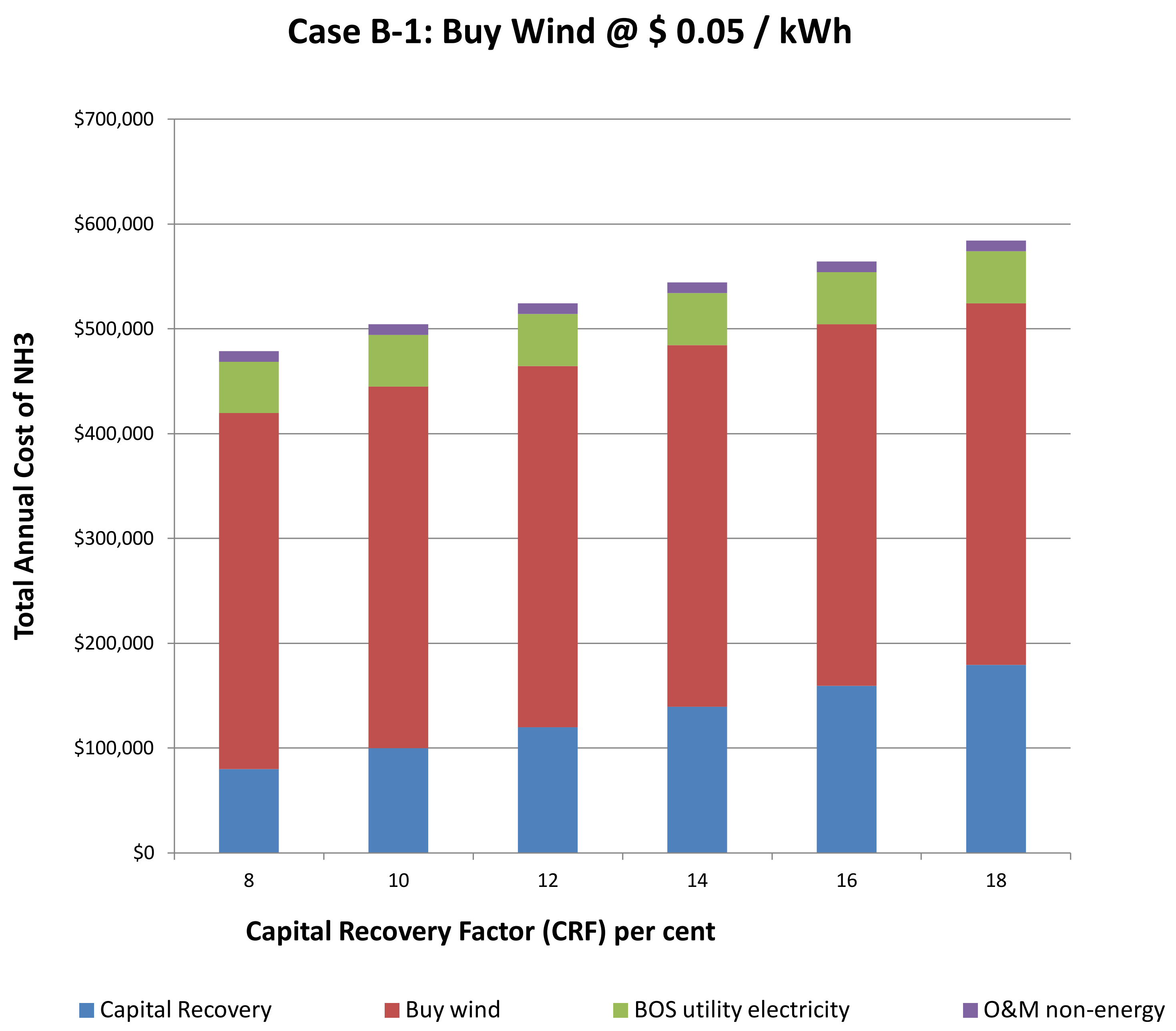

Case A-2: Self-generate Wind; no Grid Connect
$1,000,000
$900,000
$800,000
$700,000
$600,000
$500,000
$400,000
$300,000
$200,000
$100,000
$0
Total Annual Cost of NH3
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Capital Recovery
BOS Purch Elec Energy
O&M Except Elec Energy

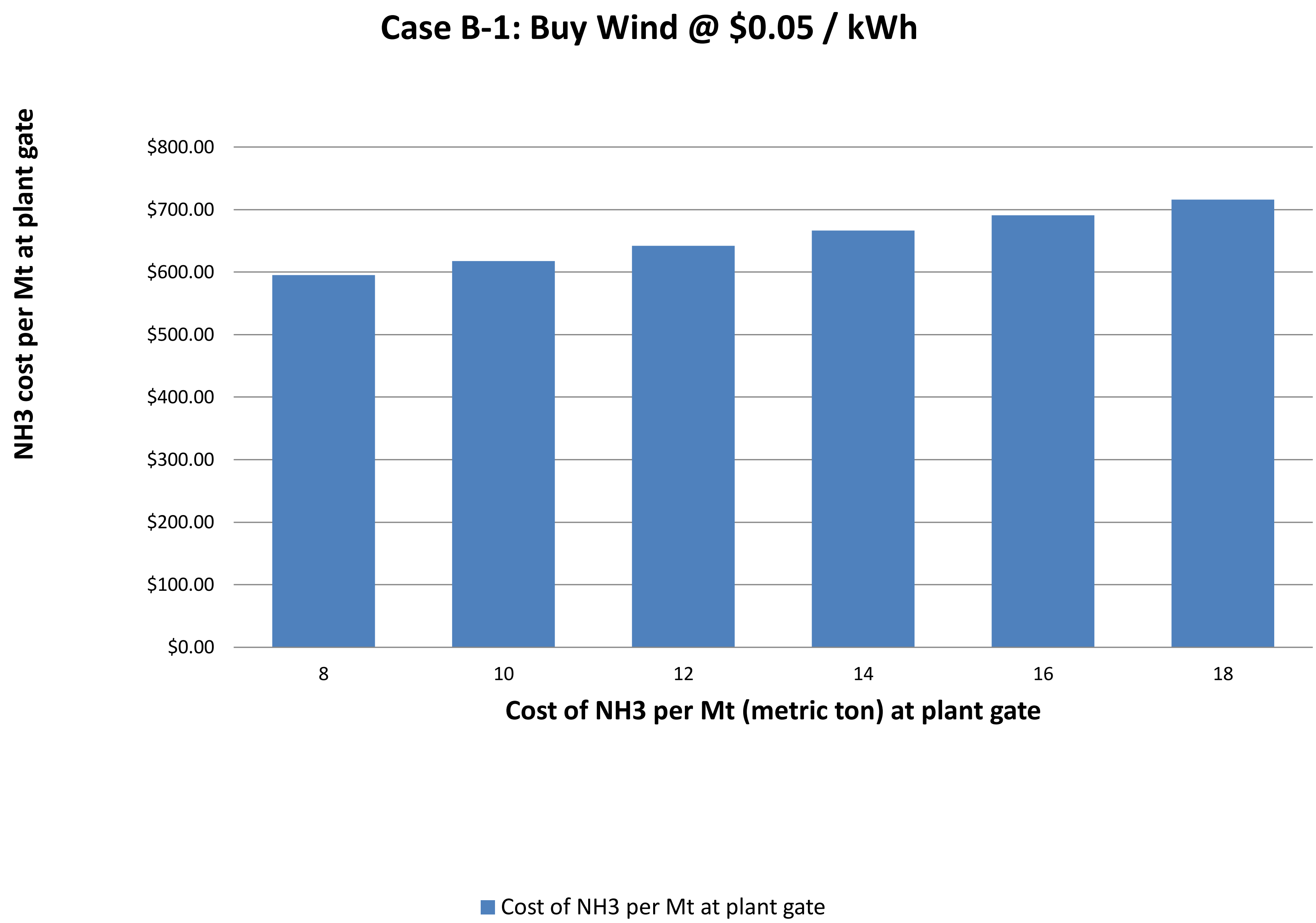
## Case A-2: Self-generate Wind; no Grid Connect

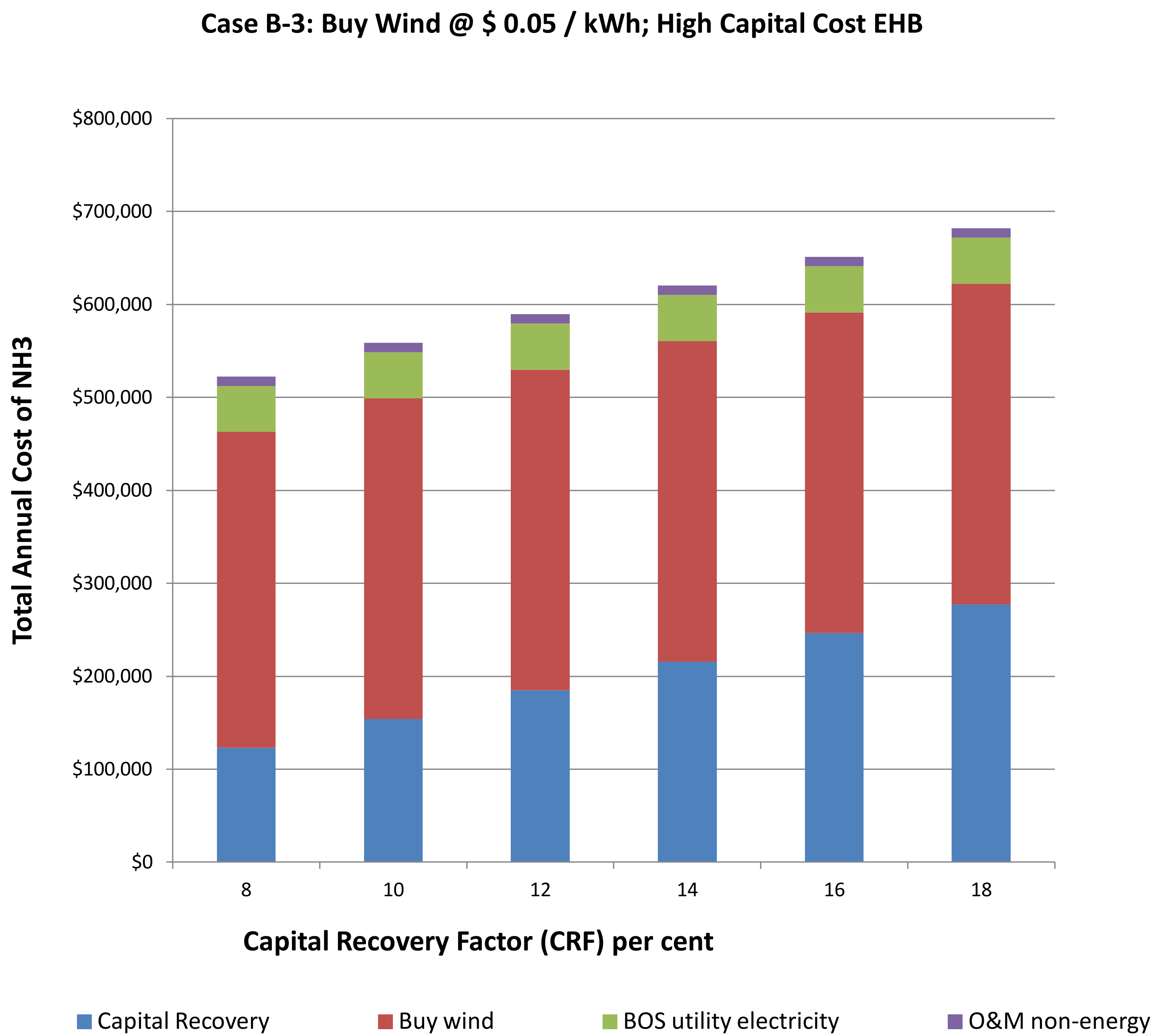


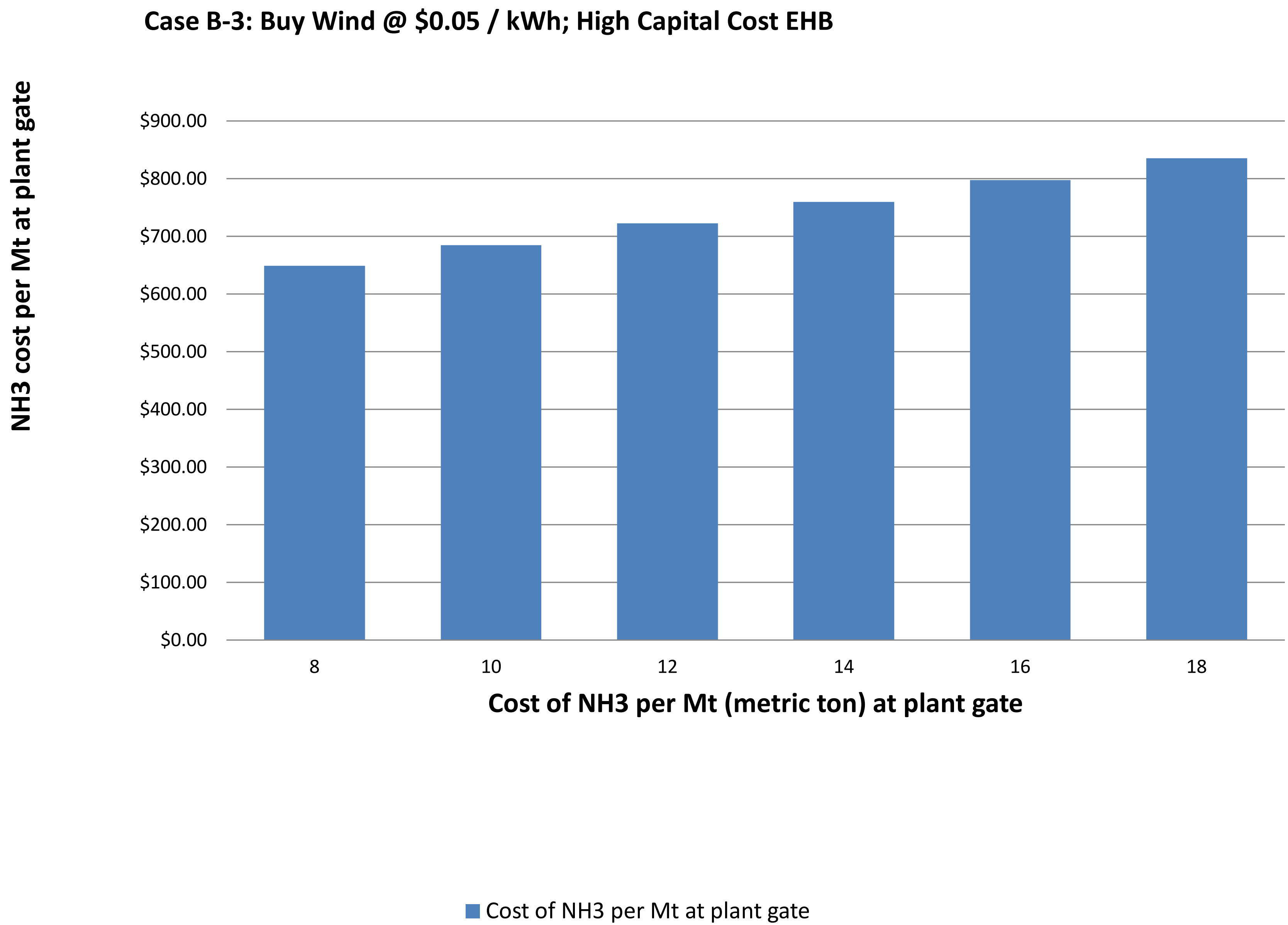

Case A-4: Self-generate Wind: High Wind AEP
Total Annual Cost of NH3
$1,400,000
$1,200,000
$1,000,000
$800,000
$600,000
$400,000
$200,000
$0
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Capital Recovery
BOS Purch Elec Energy
O&M Except Elec Energy


Case A-4: Self-generate Wind: High Wind AEP
NH3 cost per Mt at plant gate
$1,200.00
$1,000.00
$800.00
$600.00
$400.00
$200.00
$0.00
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Cost of NH3 per Mt (Metric ton) at plant gate


Case B-1: Buy Wind @ $ 0.05 / kWh
$700,000
$600,000
$500,000
$400,000
$300,000
$200,000
$100,000
$0
Total Annual Cost of NH3
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Capital Recovery
Buy wind
BOS utility electricity
O&M non-energy


Case B-1: Buy Wind @ $0.05 / kWh
NH3 cost per Mt at plant gate
$800.00
$700.00
$600.00
$500.00
$400.00
$300.00
$200.00
$100.00
$0.00
8
10
12
14
16
18
Cost of NH3 per Mt (metric ton) at plant gate
Cost of NH3 per Mt at plant gate


Case B-3: Buy Wind @ $ 0.05 / kWh; High Capital Cost EHB
Total Annual Cost of NH3
$800,000
$700,000
$600,000
$500,000
$400,000
$300,000
$200,000
$100,000
$0
8
10
12
14
16
18
Capital Recovery Factor (CRF) per cent
Capital Recovery
Buy wind
BOS utility electricity
O&M non-energy


Case B-3: Buy Wind @ $0.05 / kWh; High Capital Cost EHB
NH3 cost per Mt at plant gate
$900.00
$800.00
$700.00
$600.00
$500.00
$400.00
$300.00
$200.00
$100.00
$0.00
8
10
12
14
16
18
Cost of NH3 per Mt (metric ton) at plant gate
Cost of NH3 per Mt at plant gate

# *Conclusion*
# *Landscape: RE-source NH3*

- Alaska demo project: AASI
- Artificial Photosynthesis: UK, July '14
- Ag Ventures, Iowa: Wind → NH3 study
- Synthesis tech survey
  - From H2
  - From electricity
- ICE gensets conversion: demand demonstrate
- Complete RE-source energy systems

# *Conclusion*
# *Landscape: RE-source NH3 Synthesis*

1. H-B reactor only good candidate
   - RE - H2 + N2
   - RE electricity → electrolyzer → H2 + O2
   - Complex system: suited for Alaska deployment ?
   - MWe input scale costs, efficiency unknown

2. Beyond Haber-Bosch "BHB" Electrolytic
   - Diverse technologies
   - TRL 1 – 3
   - Less complex system than H-B and EHB ?
   - MWe input scale costs, efficiency unknown

# *Conclusion*
# *Landscape: RE-source NH3 Synthesis*

- Electricity source RE:
  - H-B reactor only good candidate
  - Electrolysis plus Haber-Bosch (EHB)
- Hydrogen source RE:
  - H-B reactor only good candidate
  - Beyond Haber-Bosch “BHB” Electrolytic
- Many technology options:
  - All TRL 1 – 3
  - Years and $ for R&D, Demo, to commercialize

# *NH3 from Renewable-source Electricity, Water, and Air: Technology Options and Economics Modeling*

## DVD's + Handouts

***Ammonia Fuel Association***
***21 – 24 September 2014***
***Des Moines, Iowa USA***


*Bill Leighty, Director*
*The Leighty Foundation*
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*907-586-1426 206-719-5554 cell*

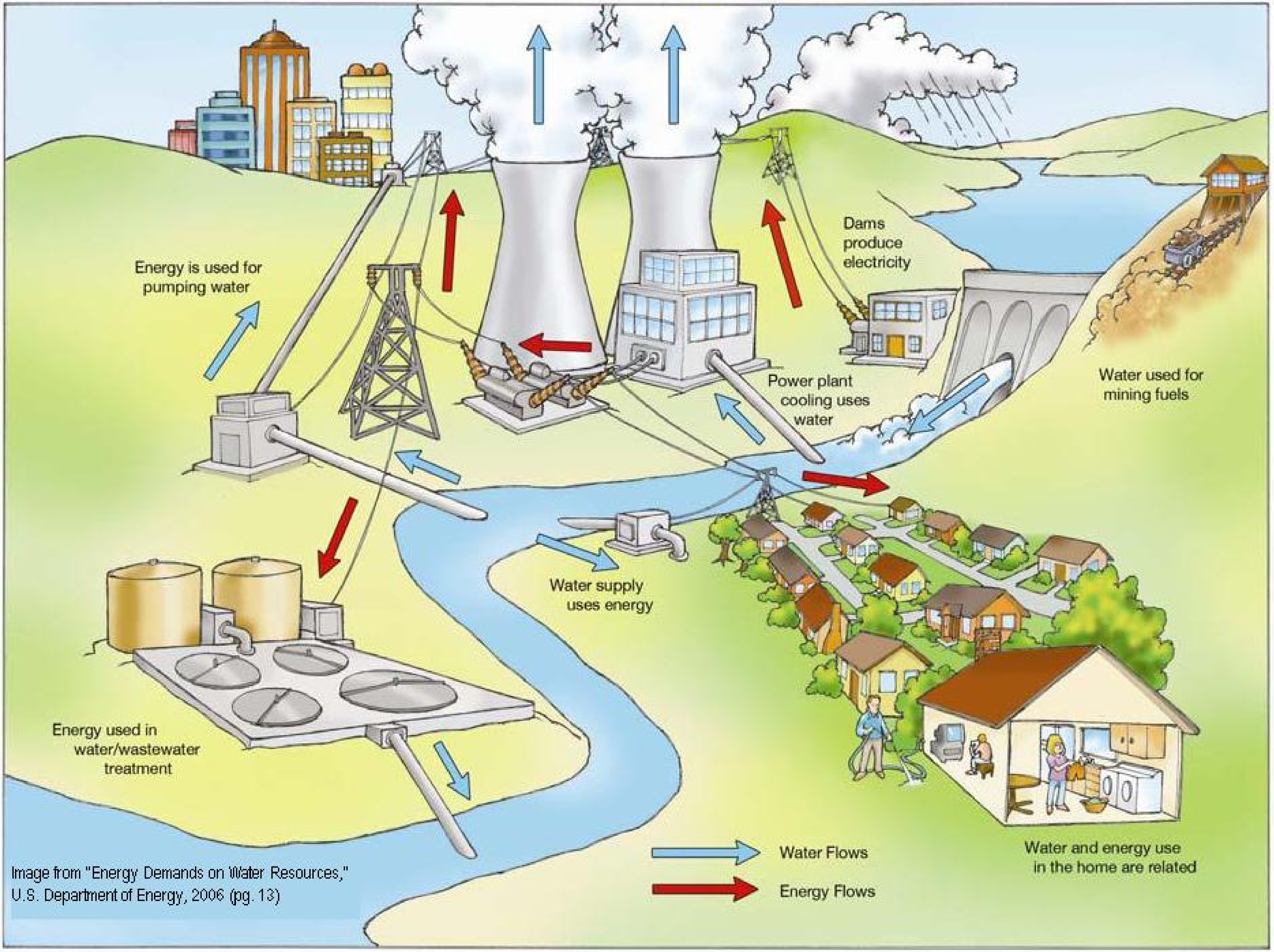


Image from "Energy Demands on Water Resources," U.S. Department of Energy, 2006 (pg. 13)