RUSS COLLEGE of Engineering and Technology

Recovery of Ammonia Energy from Municipal and Agricultural Wastewater: Ammonia Electrolysis

Gerardine G. Botte
Associate Professor, ChE
Director Electrochemical Engineering Research Laboratory

John Holbrook
Director
AmmPower LLC

Ammonia the key to US energy independence
Golden, Colorado
October 2006

OHIO UNIVERSITY

Outline

- Background
- How to get energy out?
- Ammonia Electrolysis
  - Electrolysis of ammonia effluents
  - Hydrogen Production
- Economic Analysis
- Conclusions
- Future Work

RUSS COLLEGE of Engineering and Technology

Background

- All mammals (human and animal) produce liquid and solid waste which contains considerable “undigested” energy
- Extensive activity ongoing worldwide in extracting residual energy from solids. Most visible example is anaerobic digesters, but biomass gasification and anaerobic pyrolysis (destructive distillation) also viable.
- Little R&D effort in capturing the residual energy in liquid waste, which is largely in the form of ammonia and ammonia compounds (e.g. urea)
- Mammal urine contains ~5% urea; average human excretes 3-5 liters of urine daily; average cow excretes 5-7 gallons

RUSS COLLEGE of Engineering and Technology

How to get energy out?

- Aqueous urea is chemically 2 parts NH_3 and 1 part CO_2 (overall about 8% hydrogen)
- Urea decomposes naturally at ambient temperatures to yield NH_3 via urease bacteria action, but this is a sluggish process
- Above 500F urea decomposes thermally very rapidly; this process used extensively in de-NOx (NH_3 + NOx → N_2 + H_20)
- Urea also broken down in pressurized water reactors at ~200C, but much of the energy in the urea is consumed
- Electrolysis of ammonia/urea solutions could provide a low-T, energy efficient way to get the energy out of urea

Ammonia Electrolysis: In Situ H_2 Production

- Anode: Ammonia Oxidation

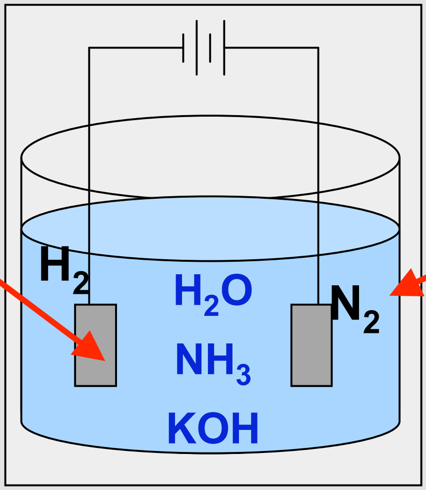
$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^- \quad \mathrm{E}^0 = -0.77 \text{ vs SHE}$$

- Cathode: Water Reduction

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \mathrm{E}^0 = 0.82 \text{ V vs SHE}$$

- Overall Reaction

$$2NH_3 \rightarrow N_2 + 3H_2 \quad \mathrm{E}^0 = 0.059 \text{ V}$$



RUSS COLLEGE of Engineering and Technology

Comparison with Water Electrolysis

Theoretical (Thermodynamics) Calculations

- Background
- How to get energy out?
- **Ammonia Electrolysis**
  - Effluents
  - H_2 Production
- Economic Analysis
- Conclusions
- Future Work

- Using Solar Energy at $0.214/kW-h
- Ammonia cost at $300 per ton metric

	Water Electrolysis	**NH_3 Electrolysis**
Energy (W-h/g H_2)	33	**1.55**
Hydrogen Cost ($/kg H_2)	7.1	**2.00**

SAVING

95% LOWER ENERGY

71 % CHEAPER H_2

RUSS COLLEGE of Engineering and Technology

Advantages of Technology

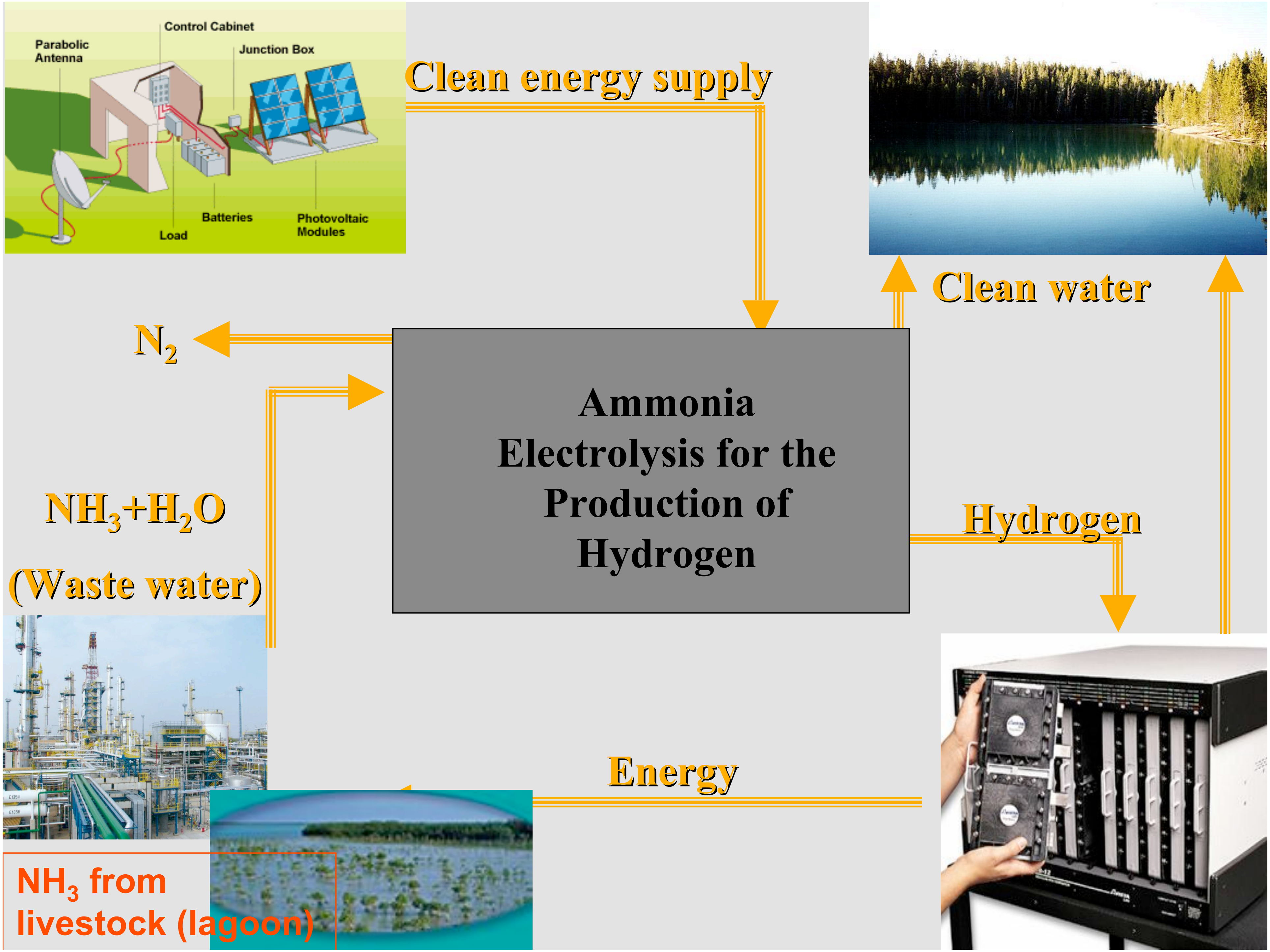
- Minimization of hydrogen storage problem
- Electrolytic on-board reforming
- Zero green house emissions
- Fuel Flexibility
- Low temperature operation
- Compatibility with renewable energy sources (e.g. solar, wind)
- Fertilizer plants, municipal waste water treatment stations, and modern engineered dairy/hog/poultry farms could potentially produce their own energy from waste

RUSS COLLEGE of Engineering and Technology

Technology Objectives

- Ammonia removal from wastewater
  - Protect rivers, lakes and groundwater
  - Protect atmosphere
  - Reduce wastewater processing costs
- Efficient hydrogen generation
  - In-situ energy production
  - Renewable source
  - Low-cost hydrogen

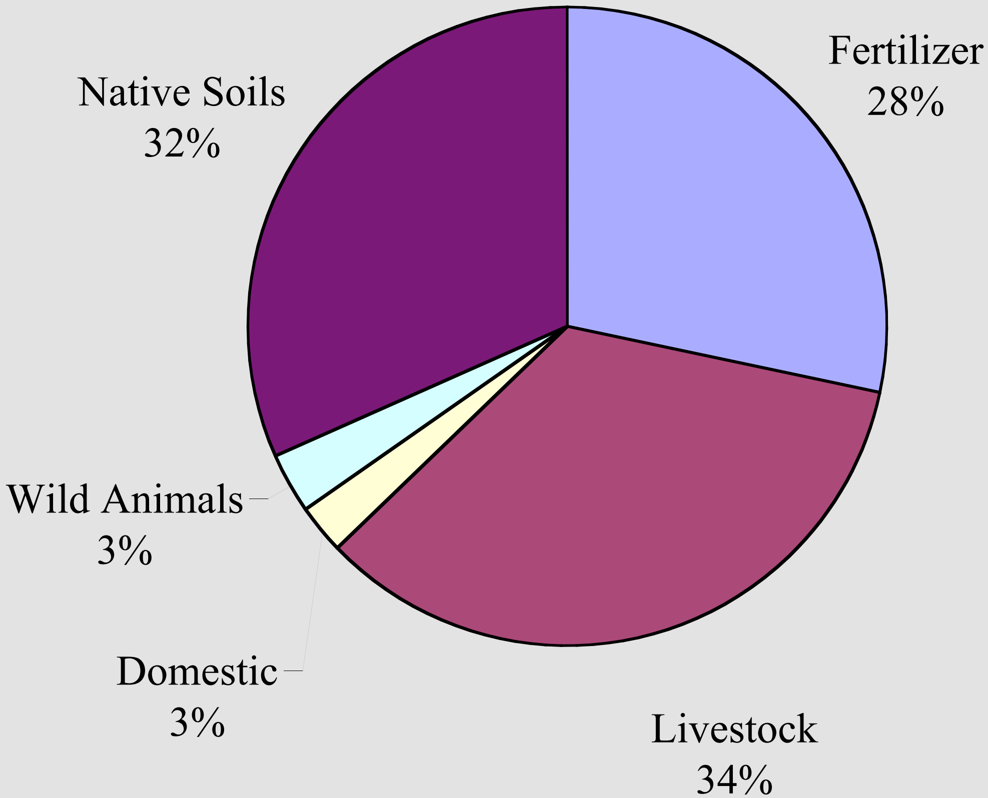
Project Vision


Control Cabinet
Parabolic Antenna
Junction Box
Batteries
Load
Photovoltaic Modules
Clean energy supply
Clean water
N2
Ammonia Electrolysis for the Production of Hydrogen
NH3+H2O
(Waste water)
Hydrogen
Energy
NH3 from livestock (lagoon)

Key Point: Electrolysis of Ammonia Effluents (why?)

Ammonia Air Emissions

- Over 5 Million Ton per year (2002)[1]



US Ammonia Production
(Million Ton per year)

- 2000: 11.8
- 2001: 9.1
- 2002: 10.1
- 2003: 8.8
- 2004: 8.9

1. G. E. Mansell, "An Improved Ammonia Inventory for the WRAP Domain (Final Report)", *ENVIRON International Corporation*, Report No. 415.899.0700, March 7 (2005)

Ammonia Air Emissions

Fertilizer, livestock, and domestic 3.25 Million Ton per year[1]

36.5% of 2004 annual production

US Ammonia Production (Million Ton per year)

- 2000: 11.8
- 2001: 9.1
- 2002: 10.1
- 2003: 8.8
- 2004: 8.9

1. G. E. Mansell, "An Improved Ammonia Inventory for the WRAP Domain (Final Report)", *ENVIRON International Corporation*, Report No. 415.899.0700, March 7 (2005)

Impact of Recovery of Effluents for H_2 Production

- Background
- How to get energy out?
- **Ammonia Electrolysis**
  - **Effluents**
  - H_2 Production
- Economic Analysis
- Conclusions
- Future Work

- Assumptions
  - Recovery of fertilizer, livestock, and residential sources
  - Use to power residential houses with a consumption of 12,000 Kw-h per house
  - Combination of solar panel with ammonia electrolytic cell (AEC)
- Impact
  - Produce enough energy to power over **900,000 residential houses per year** **if all ammonia emissions captured from fertilizer, livestock, and residential sources**
  - Minimization of **1% CO_2 emissions** coming from the residential sector **by replacing fossil fuels**

Challenges. Technology implementation

- Background
- How to get energy out?
- **Ammonia Electrolysis**
  - **Effluents**
  - H_2 Production
- Economic Analysis
- Conclusions
- Future Work

- Design Electrodes capable of electrolyzing ammonia at low concentrations
- Unknown kinetics at low concentrations of ammonia
- Unknown effect of contaminants present in waste waters (urea, proteins, salts, suspended solids, etc)
- Durability/reliability/lifetime of cells and electrodes

RUSS COLLEGE of Engineering and Technology

Objectives

- Design and evaluate electrode materials to improve kinetic performance at low concentrations of Ammonia

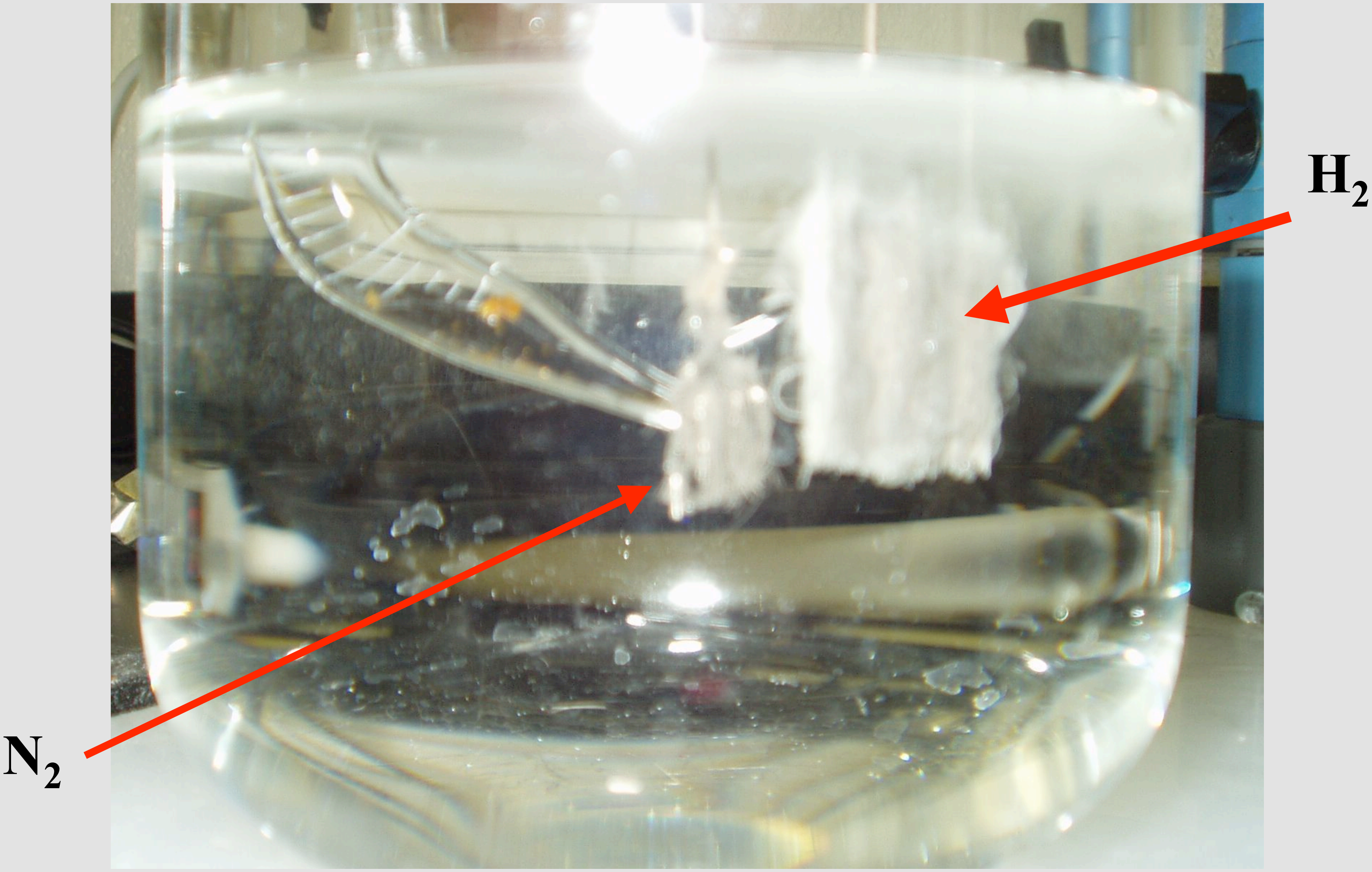
Methodology

Methodology

Substrates

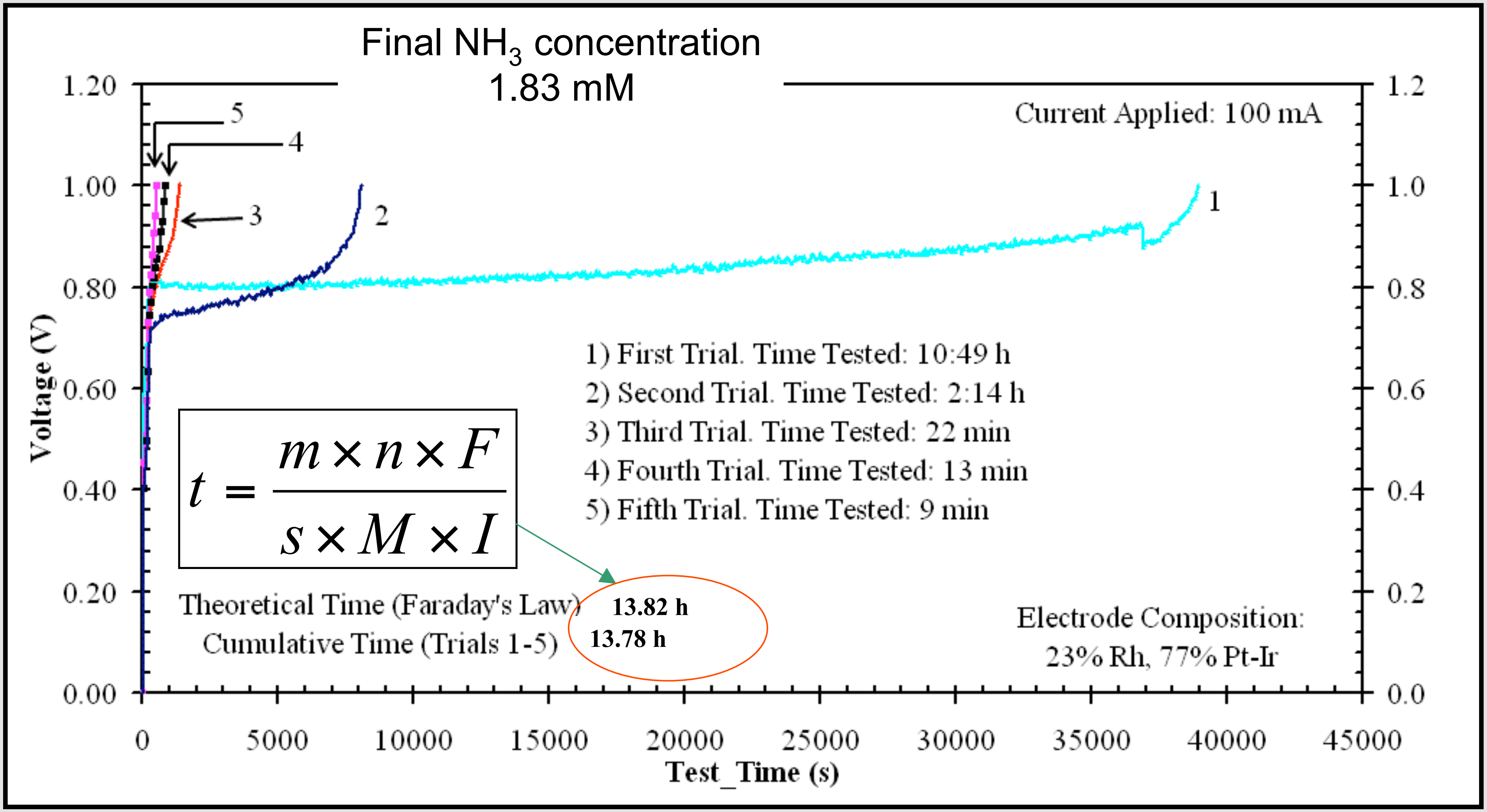
- Two different substrates tested
  - Raney Nickel
  - Carbon fibers
- Substrates plated with combinations of noble metals for the electro-oxidation of ammonia

Testing Cell



Removal of Ammonia

Performance of Pt-Ir-Rh Electrode, Initial conditions 21.5 mM NH_3 and 0.2M KOH



$$t = \frac{m \times n \times F}{s \times M \times I}$$

Faradaic Efficiency and Conversion at 25 mA/cm^2

$$x = \frac{C_o - C_f}{C_o} \times 100 \rightarrow 91.5\%$$

$$\eta = \frac{m_f}{m_t} \times 100 \rightarrow 91.8\%$$

Where:

x: conversion of ammonia

C_o: initial concentration of ammonia, mM

C_f: final concentration of ammonia, mM

η: ammonia faradaic efficiency

m_f: final mass of ammonia, g

m_t: theoretical mass of ammonia, g

Successfully demonstrated

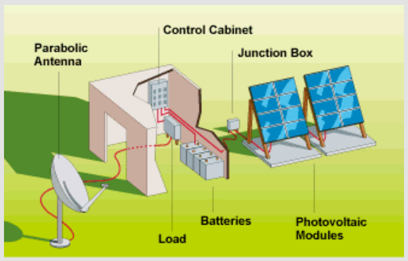
Key Point: Hydrogen Production, Ammonia as a Hydrogen Carrier

Objectives

- Evaluate the Feasibility of the technology for Distributed Size Onsite Hydrogen Production (480 kg H_2/day)
  - Energy balance
  - Economics analysis

Energy Balance

Operating Options (Day): Theoretically



Electrical Energy

1.55 W-h/g H_2

$NH_3/KOH/H_2O$

N_2

Heat

OU AMMONIA IN SITU H_2 GENERATOR

H_2

FUEL CELL

Air

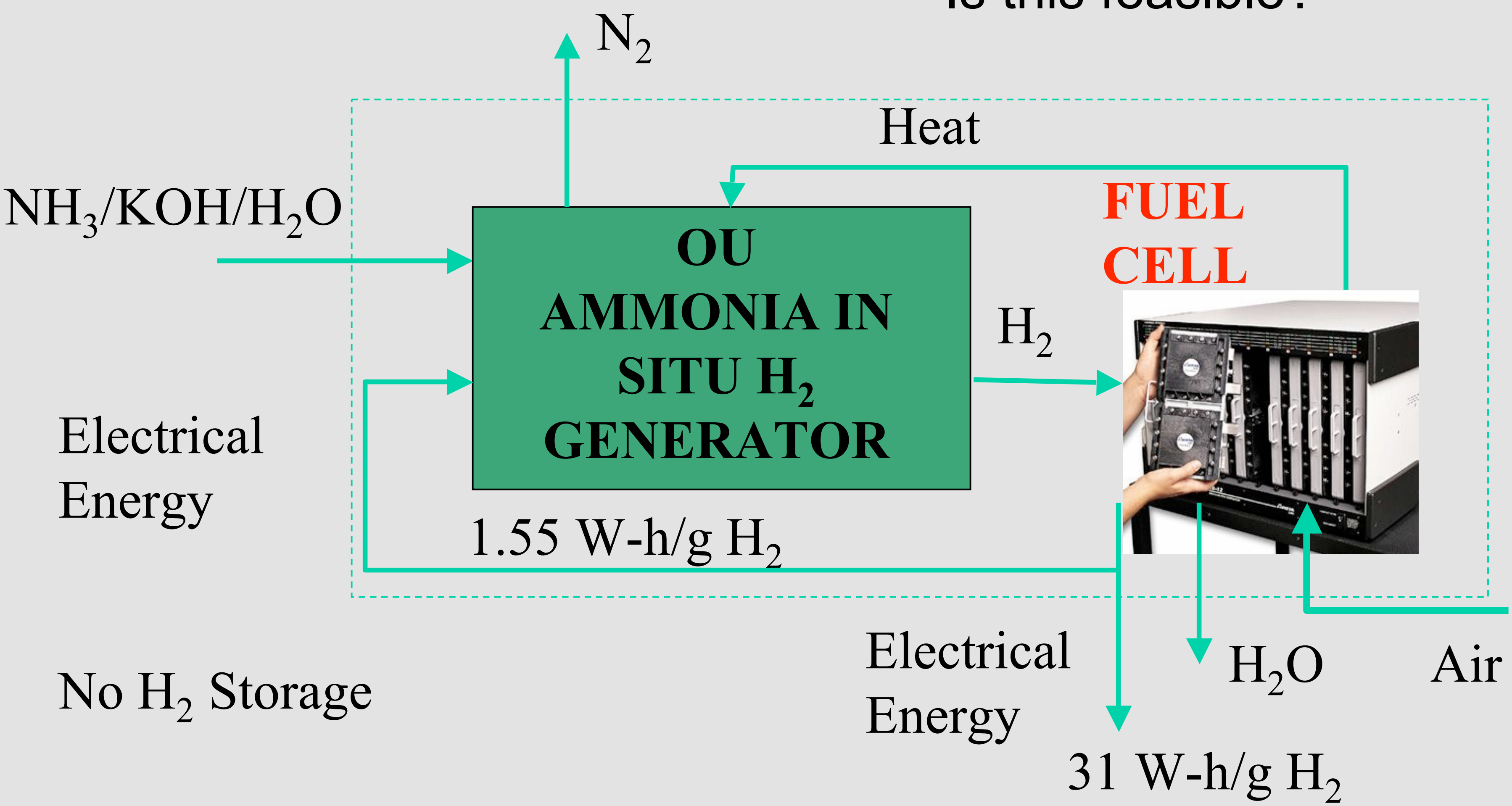
Electrical Energy

33 W-h/g H_2

H_2O

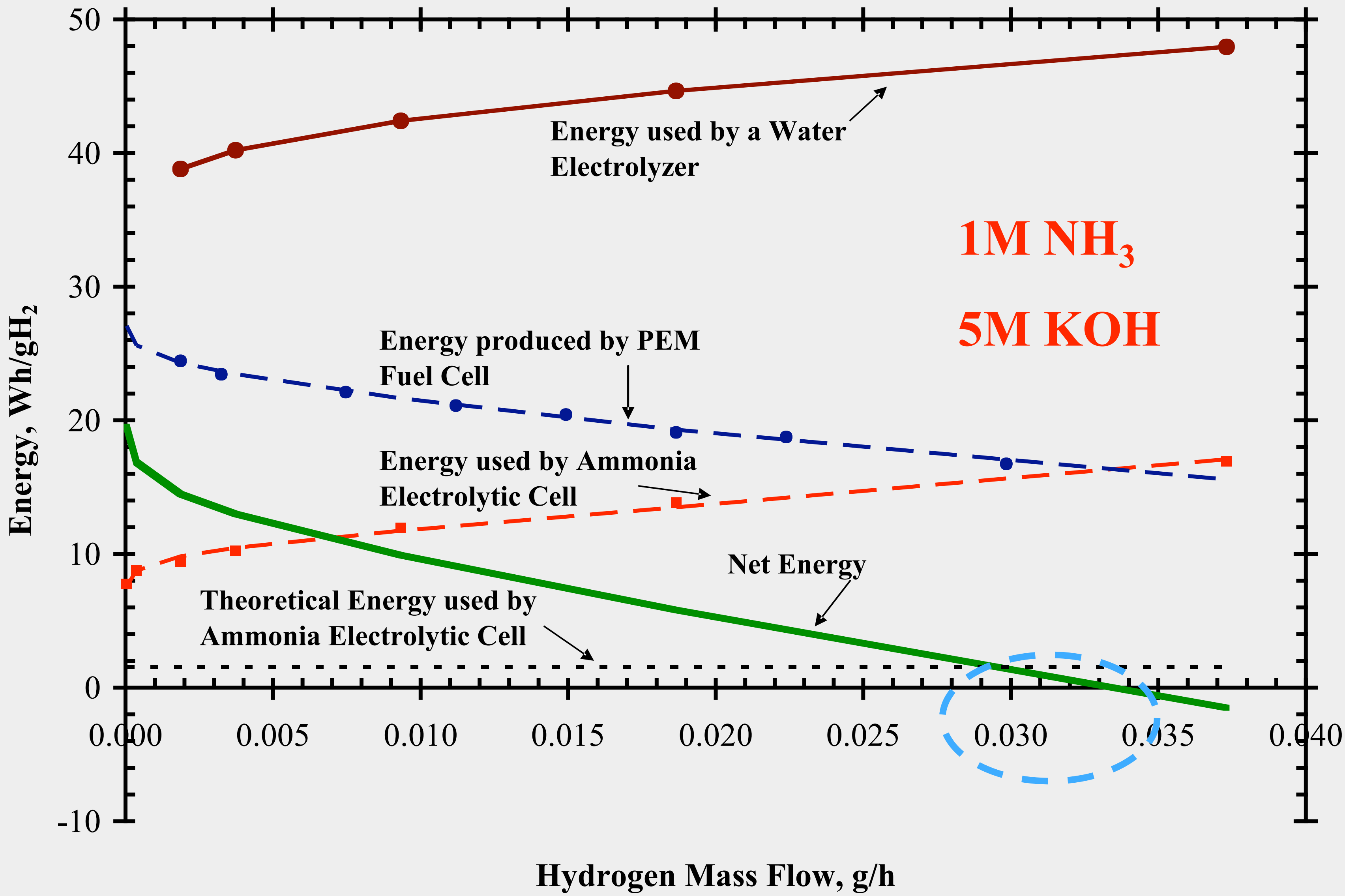
Operating Options (Night): theoretically

Is this feasible?



No H_2 Storage

Energy Balance at 25 ^oC



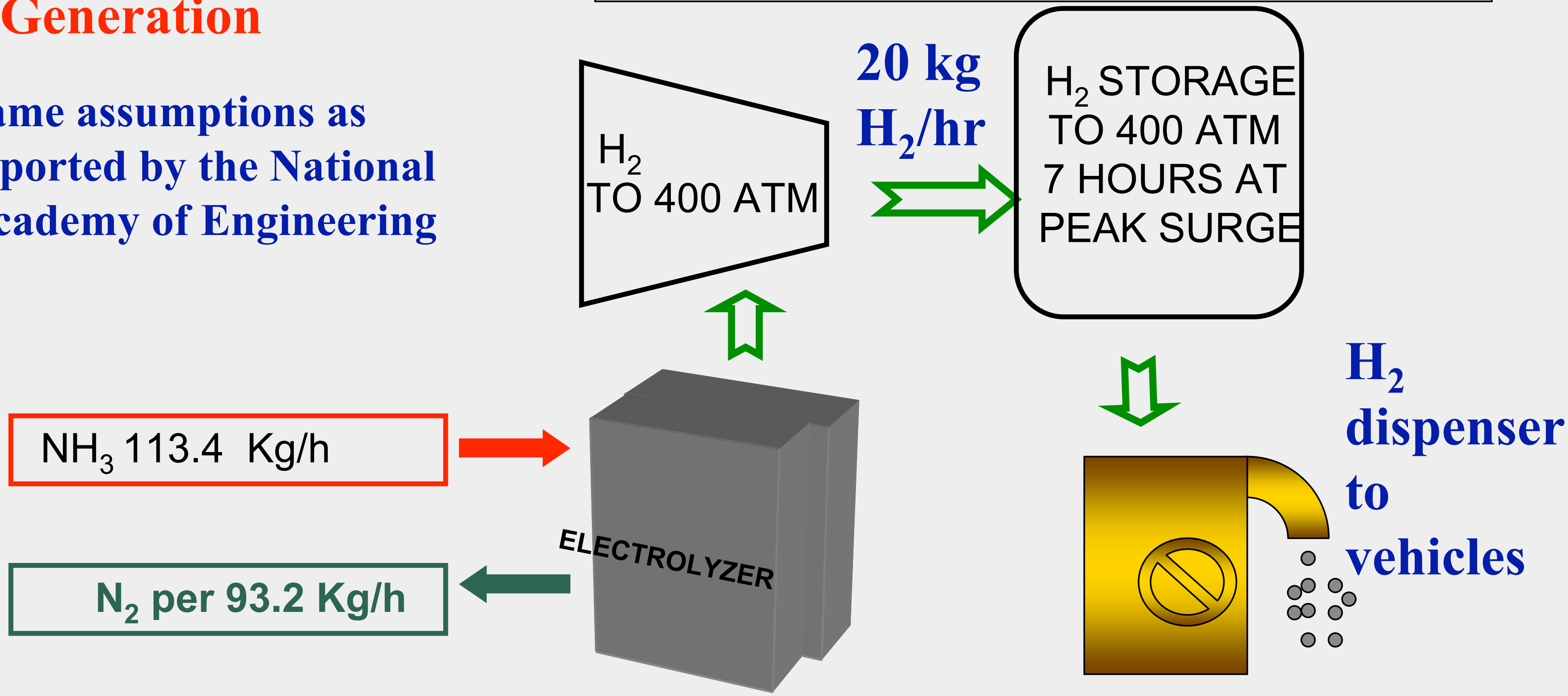
Economics Analysis and Comparison with Other Technologies for Distributed Size Onsite Hydrogen Production (480 kg H_2 per day)

1. Same assumptions as the Hydrogen Economy by the National Academy of Science
2. Cost of Ammonia $300 per Metric Ton
3. Cell Operating at 50 ^{o}C with 0.058 cell Voltage
4. Energy consumption of by electrolysis 1.55 Kw-h/kg of H_2. 100% Electric Efficiency
5. Electricity at $0.07 per kwh

Proposed System for Distributed Power Generation

CAPACITY: 480 kg H_2 per day
ANNUAL AVERAGE OPERATING LOAD: 90%

Same assumptions as reported by the National Academy of Engineering



TOTAL CAPITAL COST $ 0.743 million

CAPITAL CHARGES: $ 20,000 /year

TOTAL VARIABLE COST $ 285,000 /year

AMMONIA at $ 300 per ton

ELECTRICITY at $ 0.07 per kwh

Up to 1000 kg H_2/day

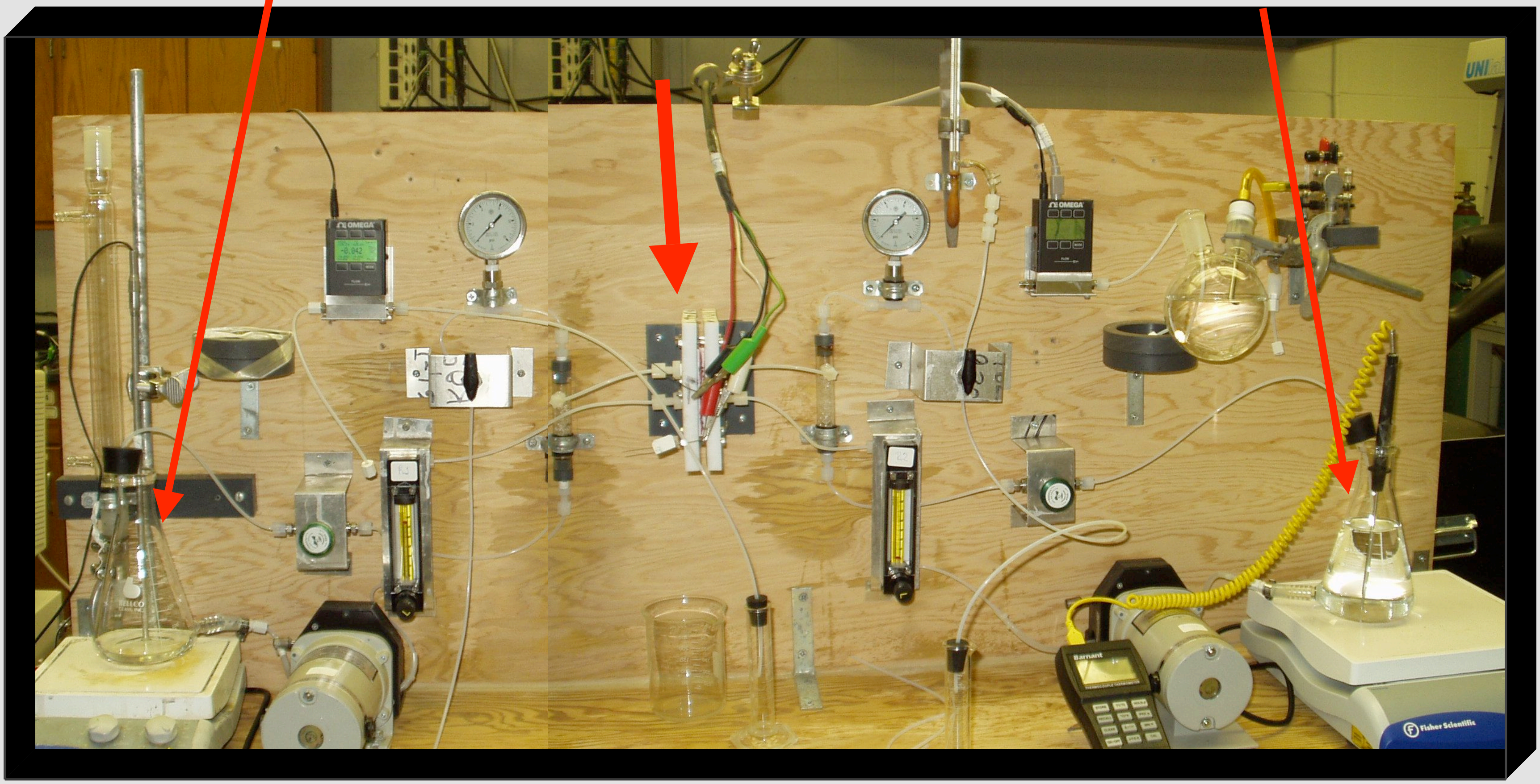
Economic Analysis at Current Operating Conditions

Testing Loop

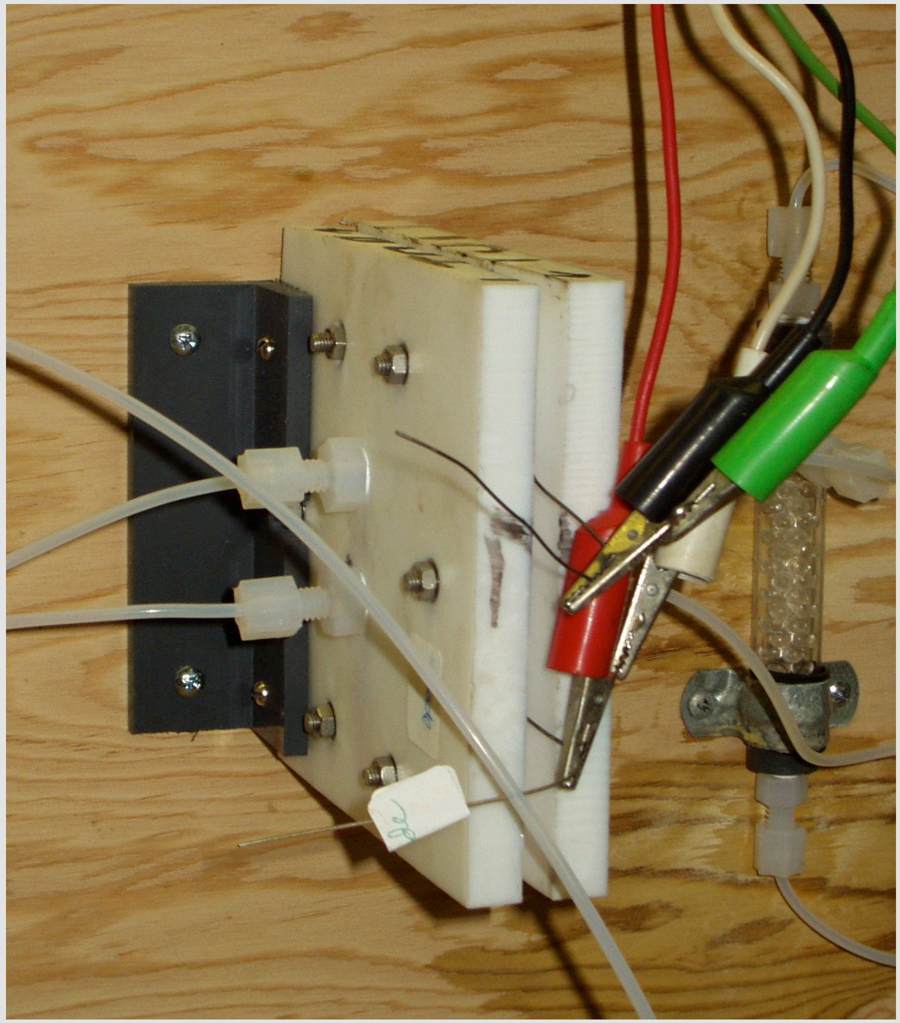
NH_3/KOH/water feed tank

NH_3 Electrolytic Cell

KOH/water feed tank



The Ammonia Electrolytic Cell



Optimization of AEC Performance

Results

Rundomized Order	KOH Concentration (M)	NH_3 Concentration (M)	Current (mA)	Temperature (°C)	Energy Consumption (W-h/gH_2)
1	0.5	0.5	300	25	**15.5**
2	0.5	0.5	100	25	**12.2**
3	0.5	5	100	25	**9.0**
4	0.5	5	300	50	**11.5**
5	7	0.5	300	50	**11.3**
6	7	5	300	25	**13.6**
7	0.5	0.5	300	50	**12.2**
8	7	5	100	50	**8.6**
9	0.5	5	100	50	**8.7**
10	7	0.5	100	50	**9.4**
11	7	0.5	300	25	**14.0**
12	0.5	5	300	25	**14.4**
13	0.5	0.5	100	50	**9.9**
14	7	5	300	50	**10.2**
15	7	0.5	100	25	**11.6**
16	7	5	100	25	**10.0**

V=0.33 V
V=0.34 V

Comparison with Other Technologies for Distributed Size Onsite Hydrogen Production (480 kg H_2 per day)

1. Same assumptions as the Hydrogen Economy by the National Academy of Science
2. Cost of Ammonia $300 per Metric Ton
3. Energy consumption based on real laboratory data
4. Electricity at $0.07 per kwh

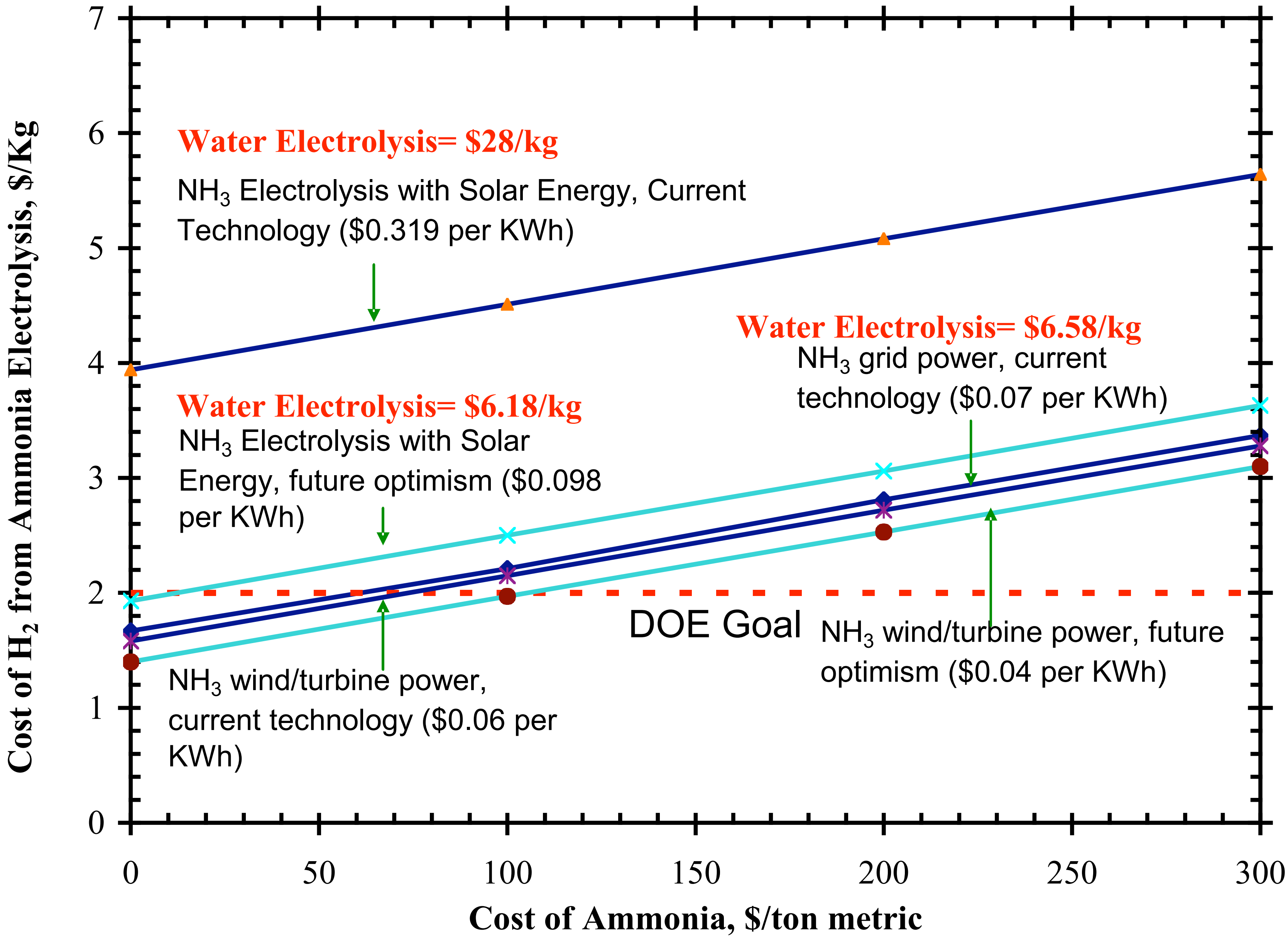
Current Technologies	Natural Gas Steam Reforming*	Water Electrolysis (52.49 Kwh/kg H_2. 75% Electric Efficiency)	**NH_3 Electrolysis** (1.55 Kwh/kg H_2. 100% Electric Efficiency	**NH_3 Electrolysis** (8.7 Kwh/kg H_2. 18.5% Electric Efficiency
Capital Investment (Million $)	1.85	2.54	**0.743**	**1.02**
Hydrogen Cost ($/kg H_2)	3.51	6.58	**2.00**	**3.37**

SAVINGS 8.2 % CHEAPER H_2 than NG reforming
48.7% CHEAPER H_2 than Water Electrolysis

At $ 0.07 KWh

Sensitivity Analysis

1. Cost of Power can change depending on the source
2. The cost of ammonia can change. If ammonia from waste is used, it is estimated that no charges will be involved
3. Current density: 25 mA/cm^2
4. Cell Operating at 50 ^{o}C with 0.34 cell Voltage



7
6
5
4
3
2
1
0
0
50
100
150
200
250
300
Cost of H2 from Ammonia Electrolysis, $/Kg
Cost of Ammonia, $/ton metric
Water Electrolysis= $28/kg
NH3 Electrolysis with Solar Energy, Current Technology ($0.319 per KWh)
Water Electrolysis= $6.58/kg
NH3 grid power, current technology ($0.07 per KWh)
Water Electrolysis= $6.18/kg
NH3 Electrolysis with Solar Energy, future optimism ($0.098 per KWh)
DOE Goal
NH3 wind/turbine power, future optimism ($0.04 per KWh)
NH3 wind/turbine power, current technology ($0.06 per KWh)

Conclusions

- Efficient removal of ammonia achieved
- Ammonia Electrolysis is much cheaper than water electrolysis
- The ammonia electrolytic cell can operated with any source of renewable energy
- H_2 can be produced at less than $2.00 per Kg for distributed power
- The economic feasibility of the technology for distributed power has been demonstrated
- The key for the process is to use ammonia from waste. In which case, up to $100 per ton metric of ammonia can be spent to purify the waste stream if needed.
- Ammonia electrolysis may be even cheaper as NO hydrogen storage tanks NEEDED.

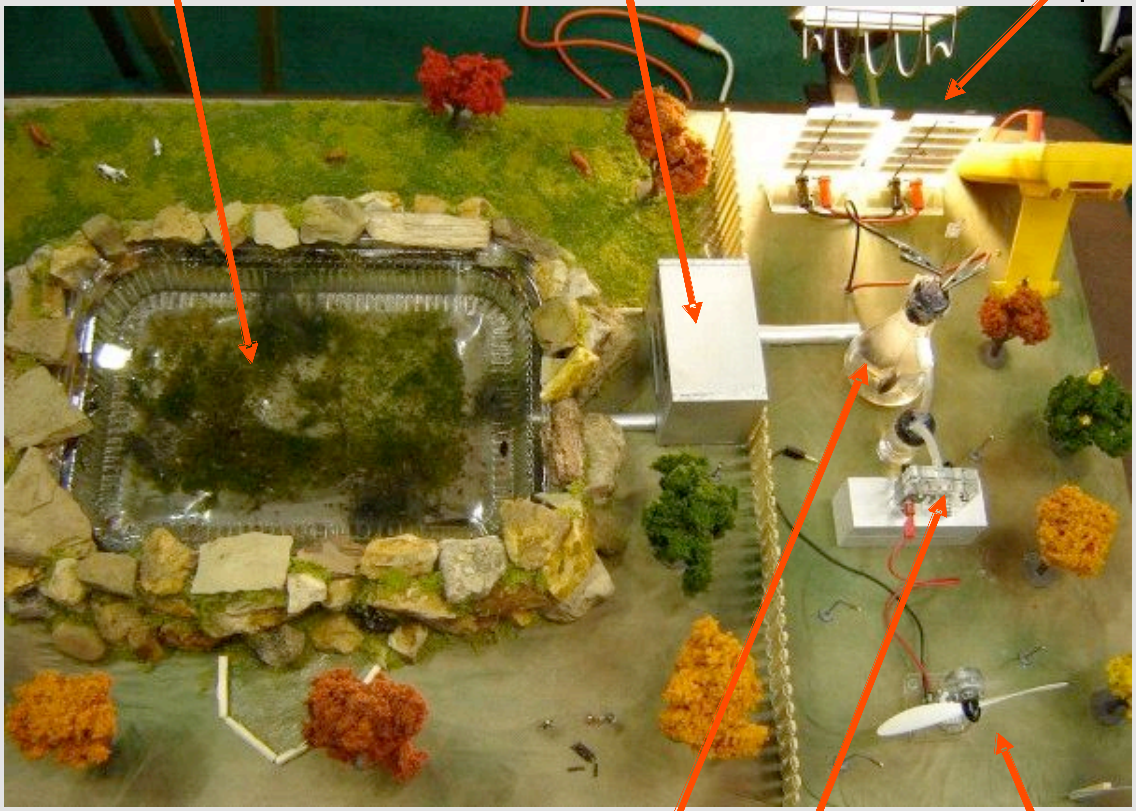
Farm of the Future

Lagoon

Pretreatment and Electrolyte Recovery Units

Sun

Solar panels



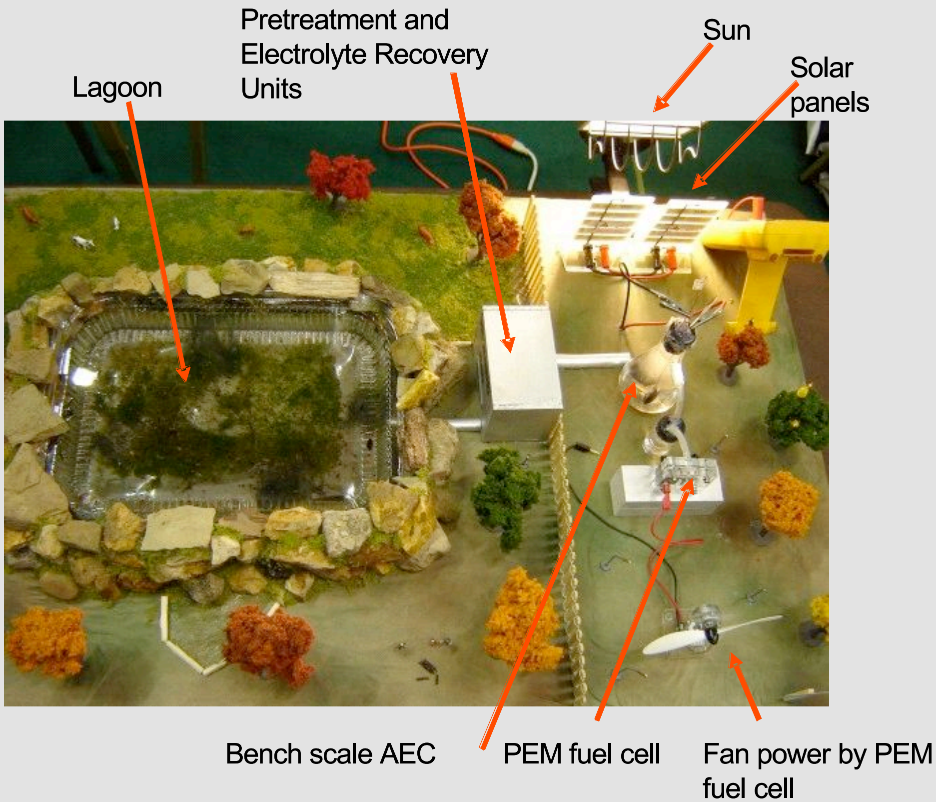
Bench scale AEC

PEM fuel cell

Fan power by PEM fuel cell

Future Work

- Improve efficiency of the process
- Determine reaction rate to scale up and design AEC to pilot scale to determine more accurate costs
- Determine energy efficiency of Power Source (integrated AEC/PEM fuel cell)
- Define pre-treatment units to use ammonia from waste



Acknowledgements

- Army Research Office (DURIP award)
- NSF Path Award
- 1804 Fund Award by the Trustees of the Ohio University Foundation Office of the Vice-President for Research, Ohio University
- Student Enhancement Award (Office of the Vice-President for Research, Ohio University)
- Dr. Ingram Department of Physics, Ohio University

The EERL Group

For more information visit:

http://webche.ent.ohiou.edu/eerl/

Contact:

Gerri Botte at botte@ohio.edu