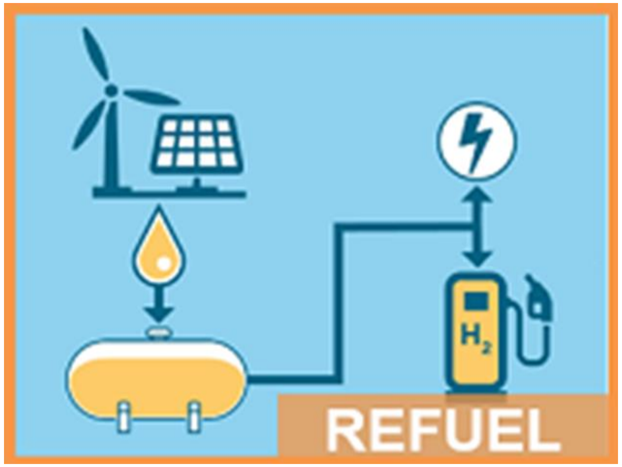
ARPA-E REFUEL Program: Distributed Production of Ammonia and its Conversion to Energy

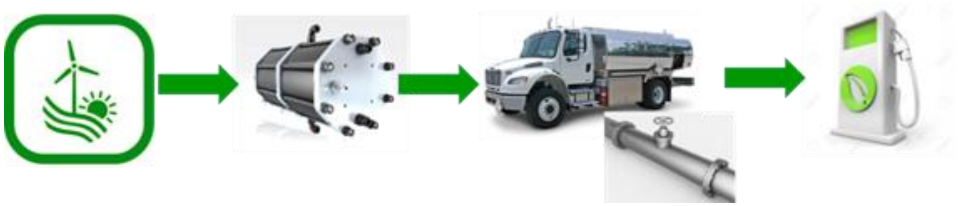
Grigorii Soloveichik
Program Director
ARPA-E



NH_3 topical conference
2019 AIChE meeting
Orlando, FL
November 13, 2019

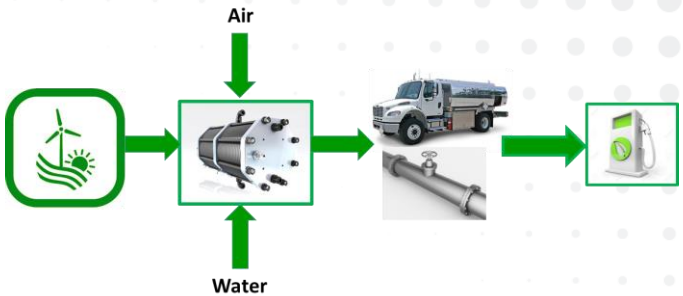
REFUEL: sustainable fuels as energy vector

1) Combine transportation and storage to reduce costs of energy from remote renewable intermittent sources to consumers, and
2) Enable the use of existing infrastructure via
i) energy conversion into hydrogen-rich liquid fuels,
ii) transportation of liquids, and
iii) energy generation at the end point using direct (combustion or electrochemical) or indirect (via intermediate hydrogen extraction) oxidation



REFUEL

Renewable Energy to Fuels through Utilization of Energy-dense Liquids



Mission

Reduce transportation and storage costs of energy from remote renewable intermittent sources to consumers and enable the use of existing infrastructure to deliver electricity or hydrogen at the end point

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Program Director	Dr. Grigorii Soloveichik
Year	2017
Projects	16
Total Investment	$33 Million

Investment areas and impacts

1. **Area: Small- to medium-scale synthesis of energy-dense carbon-neutral liquid fuels using water, air, and renewable energy source.**
   Impact: Develop technologies to produce fuels at cost <$0.13/kWh to enable long term energy storage.

2. Area: Electrochemical processes for generation of hydrogen (2a) or electricity (2b) from energy-dense carbon-neutral liquid fuels.
   Impact:
   a) Develop catalytic or electrochemical fuel cracking to deliver hydrogen at 30 bar at the cost < $4.5/kg enabling hydrogen fueling stations;
   b) Develop fuel cell technologies for conversion of fuels to electricity with source-to-use cost <$0.30/kWh .

REFUEL+OPEN

Portfolio – technology matrix ammonia synthesis

Thermal (catalytic) processes	Synthesis		Cracking
	Equilibrium shift	Reactor design	Membrane
Hydrogenation catalyst (e.g. Haber-Bosch)	M; School of Mines 1874 Colorado	RTI International	Bettergy Clean Energy for Better Life; Rensselaer
Physical effects (e.g. plasma)	SYZYGY PLASMONICS		

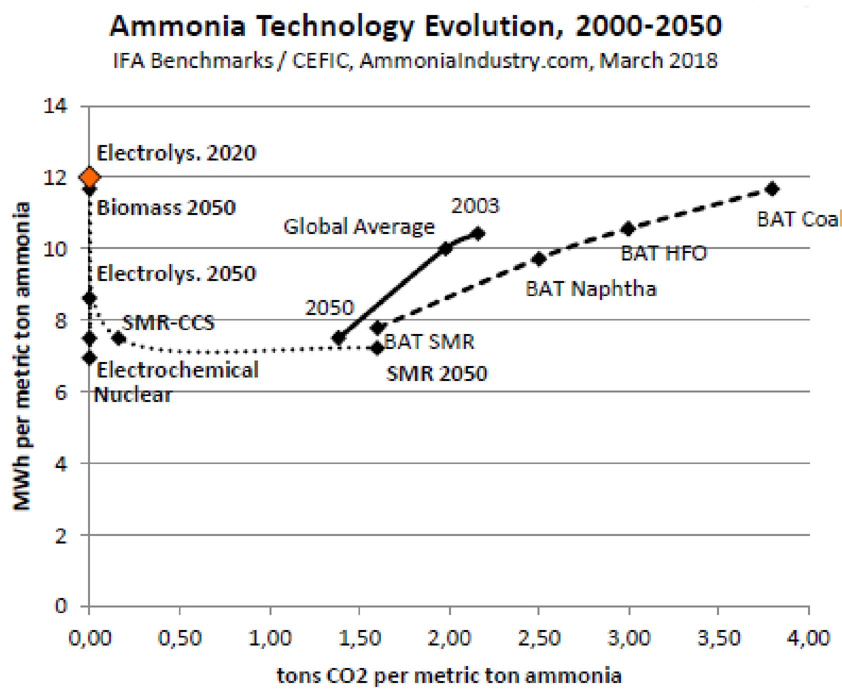
Electrochemical processes	Synthesis		Cracking
	PEM	AEM	Echem compressor
Low temperature (<120 C)	FuelCell Energy; parc A Xerox Company	WSU; GINER; storaGENergy technologies	
High temperature (>250 C)	CERAMATEC TOMORROW'S CERAMIC SYSTEMS		

Drivers for green ammonia production

- **Sustainability:** shift from natural gas or coal as a hydrogen and energy source in ammonia production to water and renewable energy to eliminate carbon emissions
- **Distributed production**: sizing and modifying the ammonia plants to match renewable energy intermittent inputs rather than fossil energy inputs to reduce transportation cost
- **Economic viability**: reducing the capital costs via mass manufacturing of modular systems to be competitive with the incumbent technology
- **Increasing energy efficiency:** using less energy (including feedstock) to produce the same quantity of ammonia

Drivers for improved ammonia production

- **Sustainability:** shift from natural gas or coal as a hydrogen and energy source in ammonia production to water and renewable energy to eliminate carbon emissions
- **Distributed production**: sizing … plants to match renewable energ… than fossil energy inputs to red…
  - Ammonia synthesis constitute 1.44% of global CO_2 emissions
  - The global average is 2.86 ton CO_2 /ton NH_3
  - The most efficient plants generate1.6 ton CO_2 /ton NH_3
  - "Green" ammonia potentially eliminates the most emissions
- **Economic viability**: reducing … costs of any new modular syst… incumbent technology
- **Increasing energy efficiency** … feedstock) to produce the sam…



Drivers for improved ammonia production

- **Sustainability:** shift from natural gas or coal as a hydrogen source in ammonia production to water and from fossil to renewable energy to eliminate carbon emissions
- **Distributed production**: sizing and modifying the ammonia plants to match renewable energy intermittent inputs rather than fossil energy inputs to reduce transportation cost

Yara BASF Ammonia Plant, Freeport Verbund, TX

Siemens Green Ammonia Demonstrator at the Rutherford Appleton Laboratory (UK)

Drivers for improved ammonia production

- Sustai ... hydrogen
  source ... ossil to
  renewa
- Distrib ... ammonia
  plants ... its rather
  than fo ... cost
- **Econo ... mass
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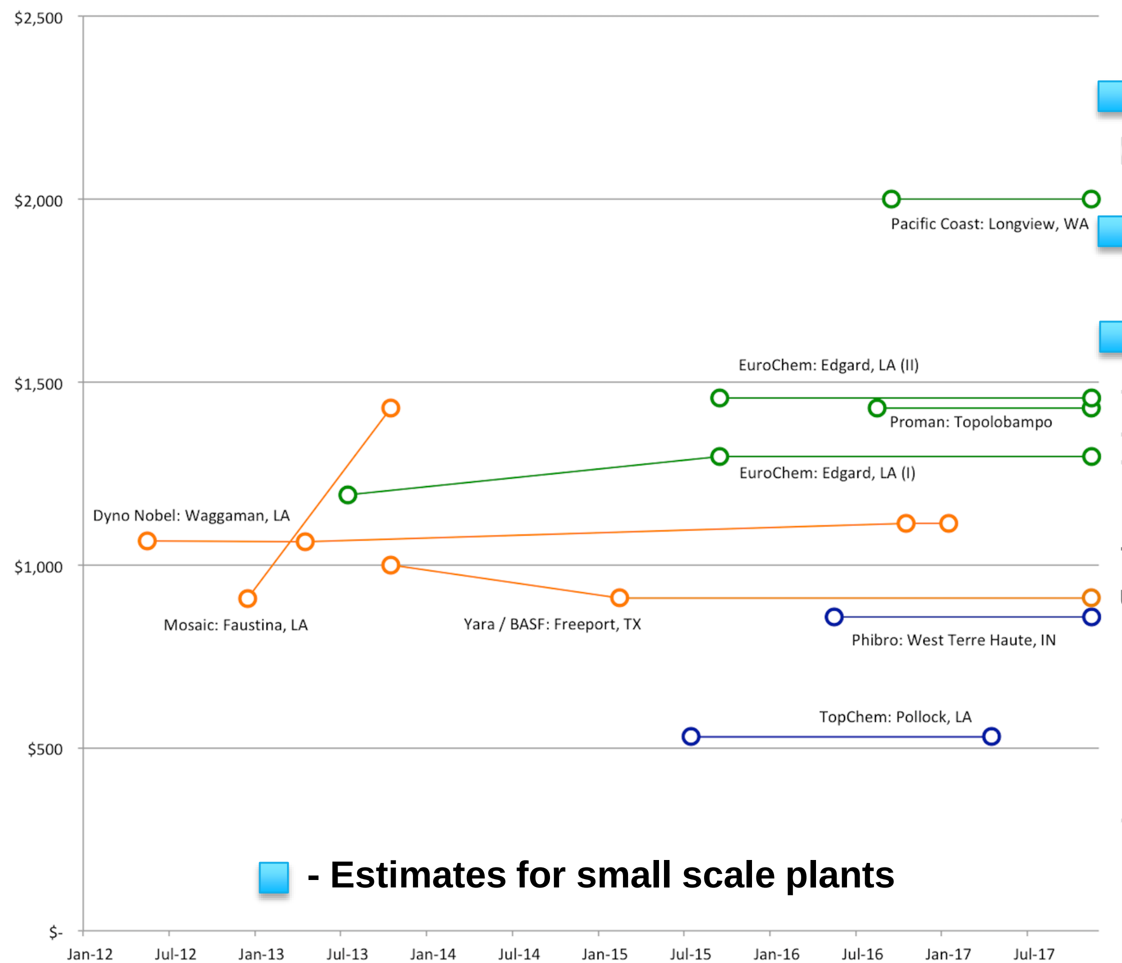
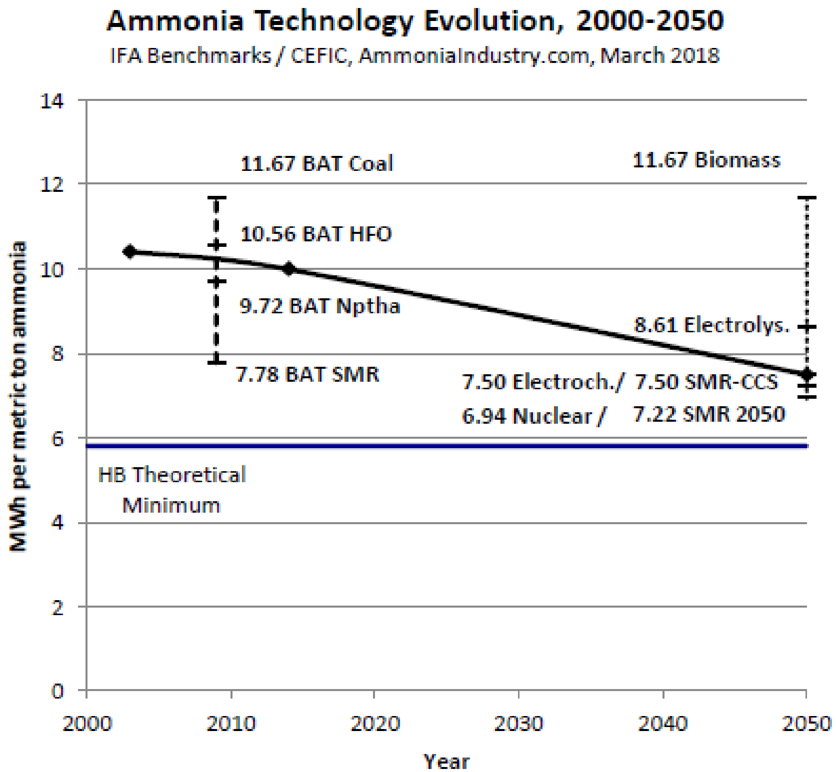


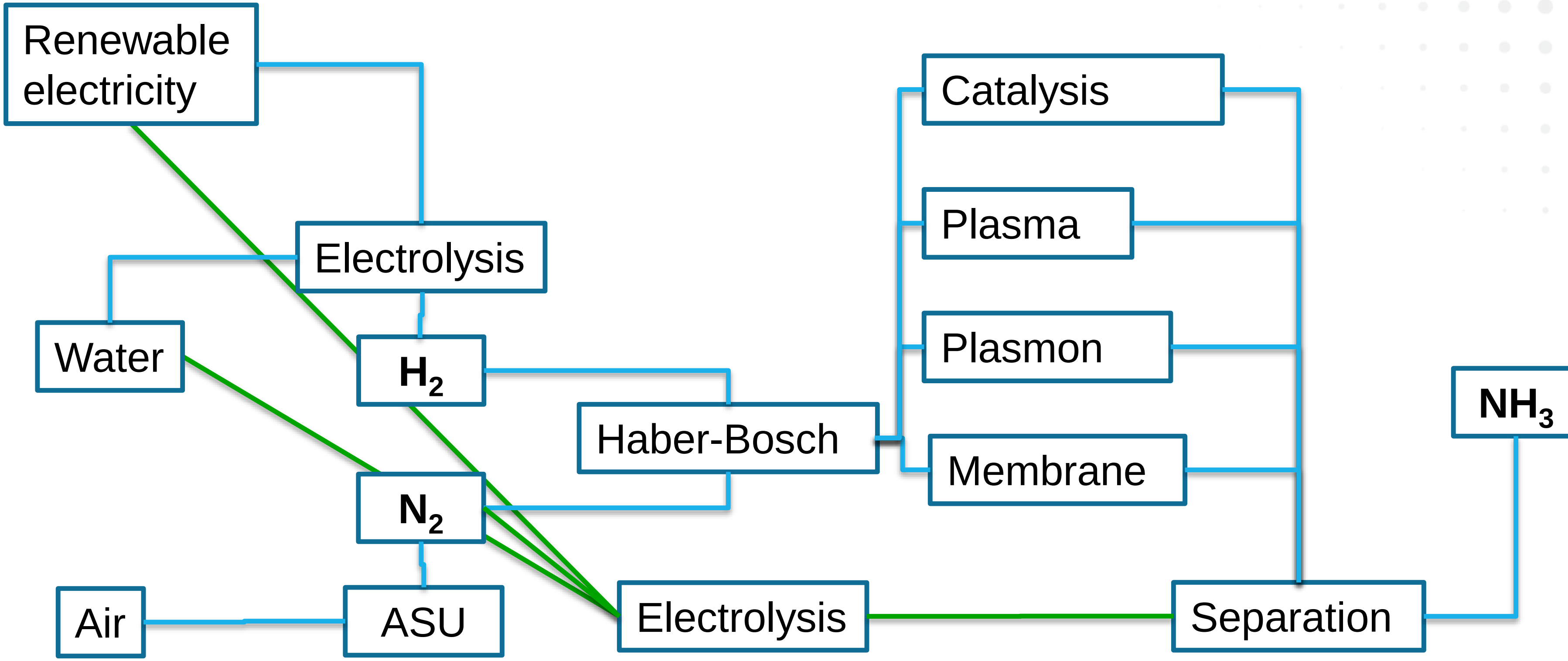
T. Brown, Ammonia Industry, 2018

Drivers for improved ammonia production

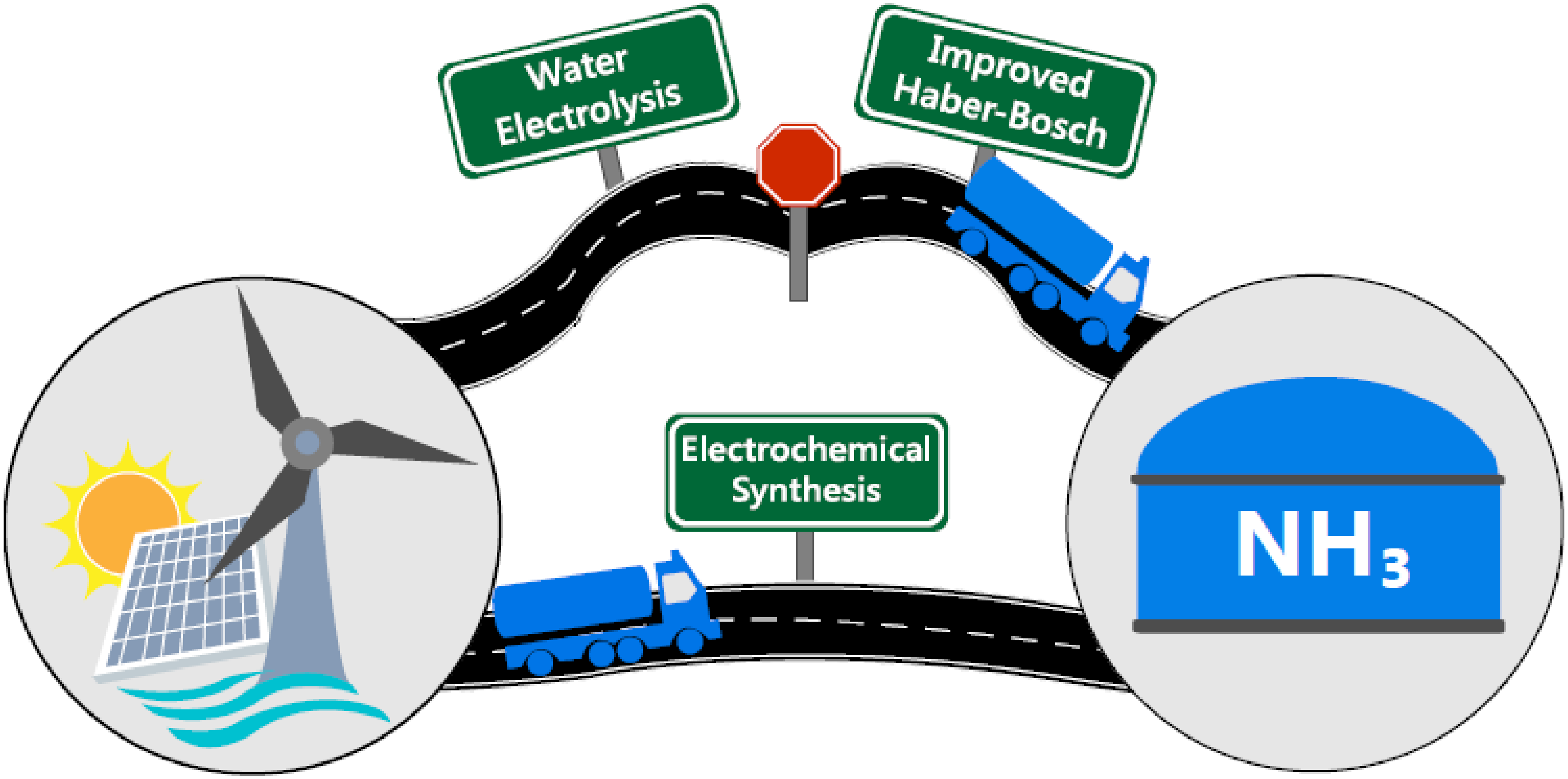


- **Sustainabili** … as a hydrogen source in am … om fossil to renewable er … ons
- **Distributed** … the ammonia plants to mat … inputs rather than fossil er … tion cost
- **Economic v** … operating costs of any … etitive with the incumbent te …
- **Increasing energy efficiency:** using less energy (including feedstock) to produce the same quantity of ammonia

Ammonia synthesis pathways



Ammonia synthesis pathways

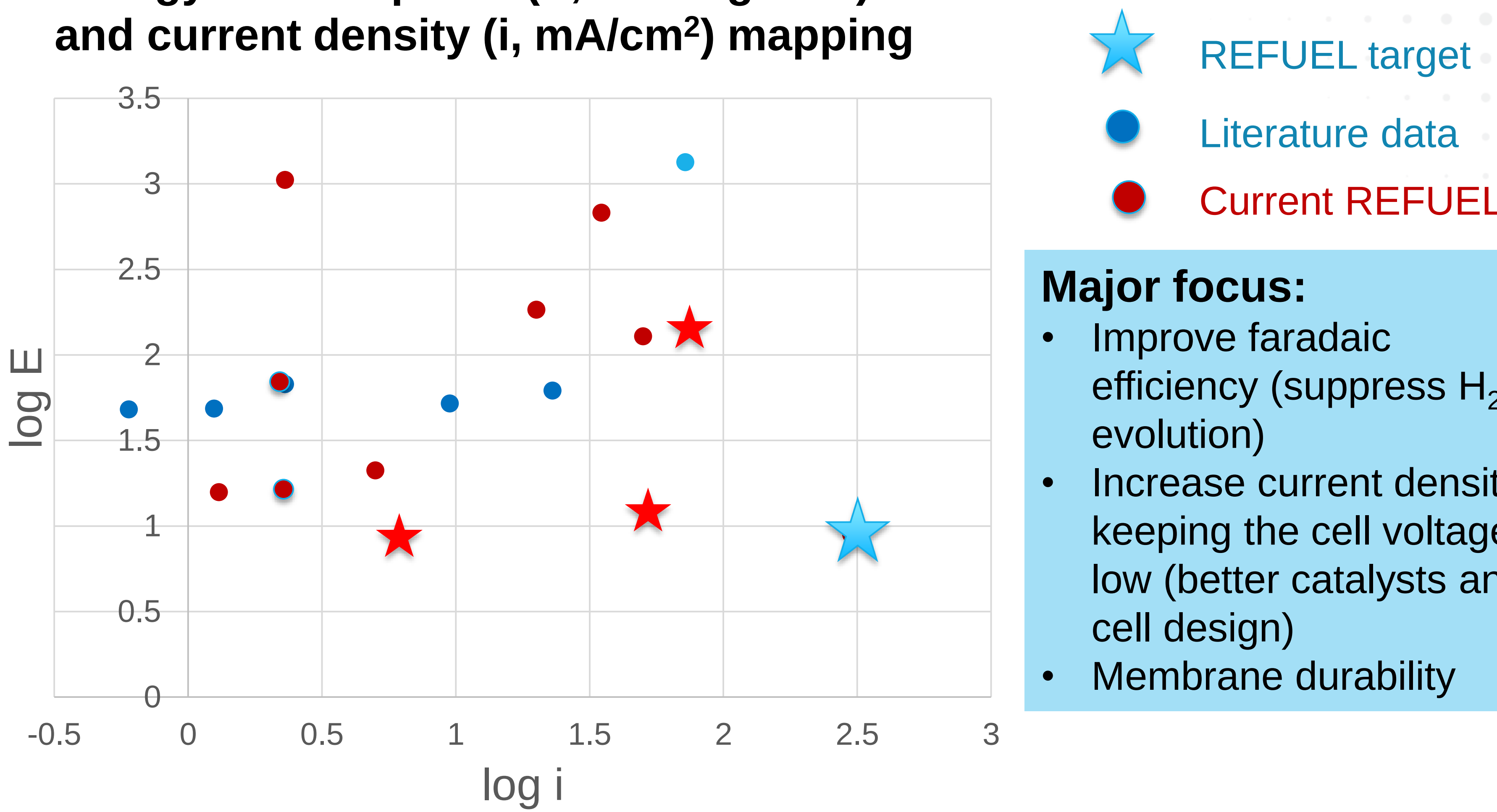


How to improve ammonia production?

- **Better, scalable Haber-Bosch process at lower temperature and pressure combined with water electrolysis**
  - drop-in developed technology, eliminates emissions
  - more active catalysts and effective ammonia removal needed
  - not suited for transient operations
- **Replace pressure and temperature with other activation methods (e.g. plasma)**
  - ability to follow the load
  - energy consumption may be unacceptable
  - scalability is unknown
- **Direct electrochemical ammonia production by co-electrolysis of nitrogen and water**
  - potentially lowest energy consumption
  - easy load following
  - low faradaic efficiency at industrial current densities

REFUEL program status: NH_3 synthesis (echem)

Energy consumption (E, kWh/kg NH3) and current density (i, mA/cm^2) mapping



Major focus:

- Improve faradaic efficiency (suppress H_2 evolution)
- Increase current density keeping the cell voltage low (better catalysts and cell design)
- Membrane durability

ARPA-E CHANGING WHAT'S POSSIBLE

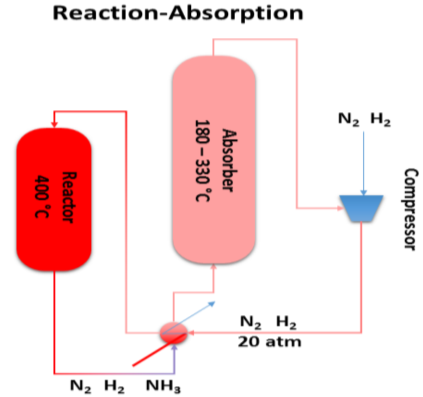
More fundamental studies needed

Haber-Bosch process improvement

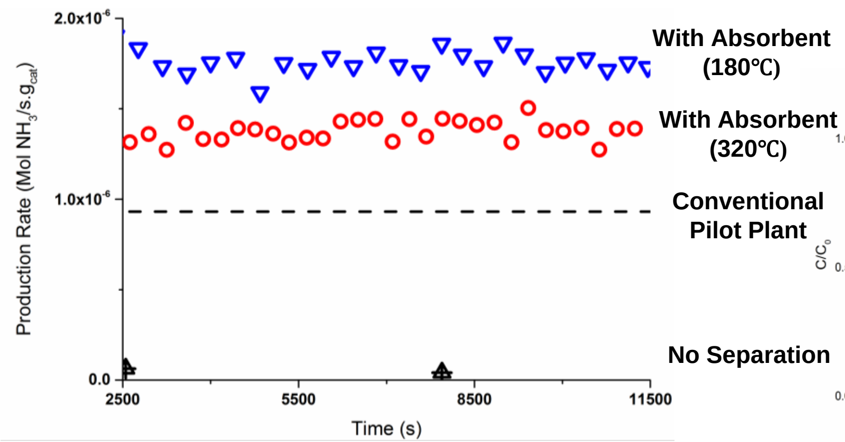
Wind to Ammonia

Project vision
Lower pressure synthesis for distributed production

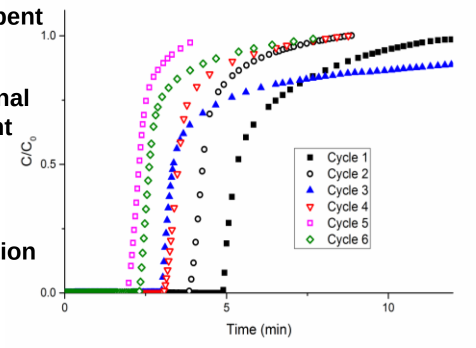
Innovation
- Replace condenser with hot solid absorbent
- Minimize compression and heat exchange
- Stabilize the absorbents with support



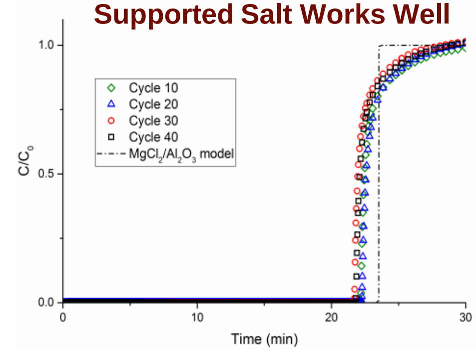
Faster Synthesis at Lower Pressure



Unsupported Salt Works Poorly



Supported Salt Works Well



Data courtesy A. McCormick, U Minnesota

DOI:10.1021/acssuschemeng.7b03159

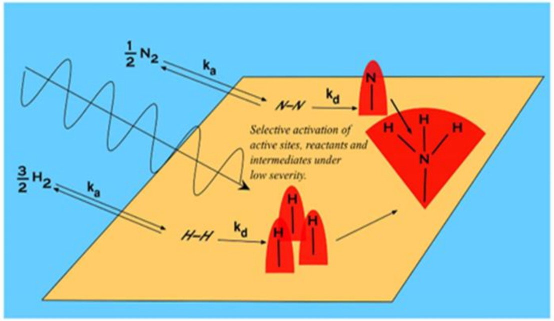
Website: https://z.umn.edu/ammonia

A. MacCormick, University of Minnesota

Renewable Energy to Fuels through Microwave-Plasma Catalytic Synthesis of Ammonia

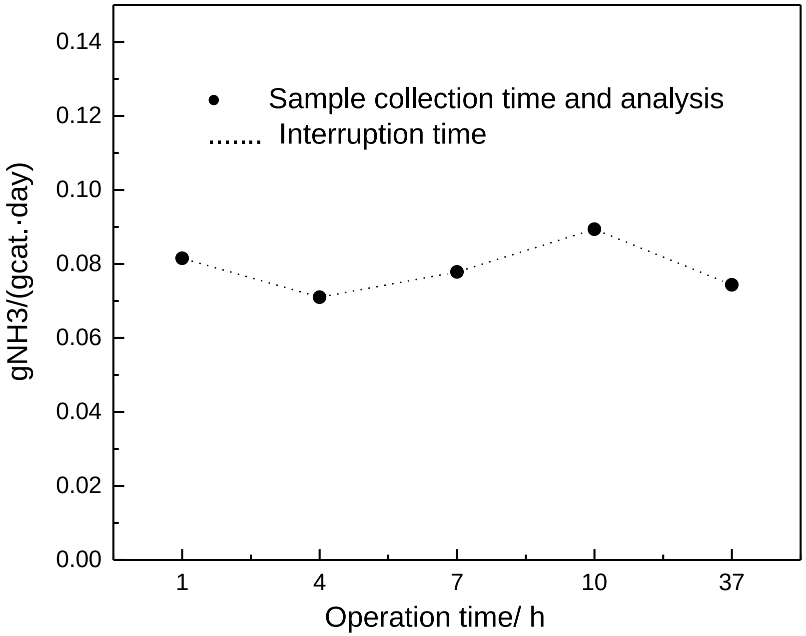
Technology

- Synergistically integrates microwave reaction chemistry with novel heterogeneous catalysis
- Decouples dinitrogen molecular activation from catalytic surface reaction.
- Changes reaction pathway at local catalytic sites, resulting in increase in reaction rate and energy efficiency.



Current status

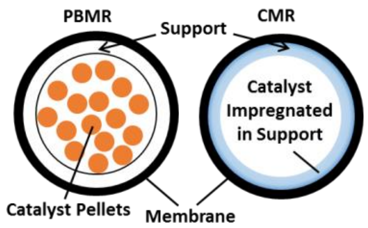
At 280°C and 1 atm, single pass N_2 conversion 3.5%, NH_3 concentration in reaction mixture ~1.8%



John Hu, West Virginia University
NETL, PNNL, FSU, Lambda Technologies, Koch Industries

Membrane Reactor Synthesis of Ammonia at Moderate Conditions

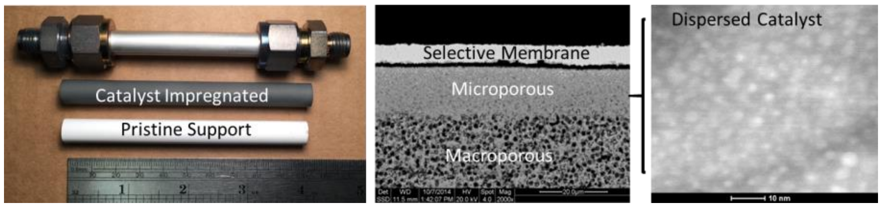
Catalytic Membrane Reactor



Catalyst-Membrane proximity

Mitigates transport limitations

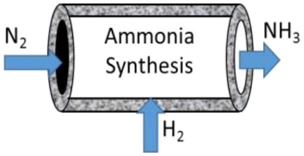
High dispersion, low loading



Technology

Use of dense, high permeable BCC metal membranes coupled to two independently optimized catalysts for H2 dissociation and N2 dissociation/NH3 formation, respectively.

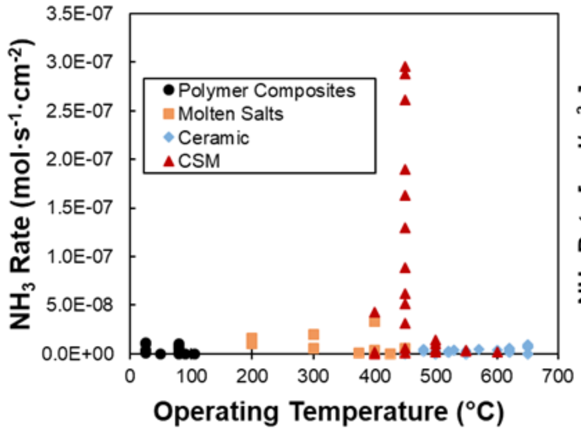
Ammonia Synthesis

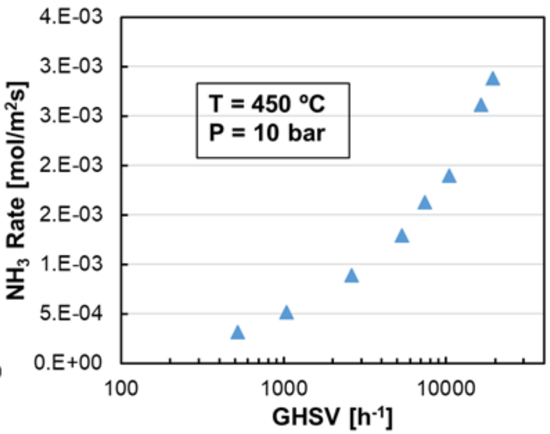


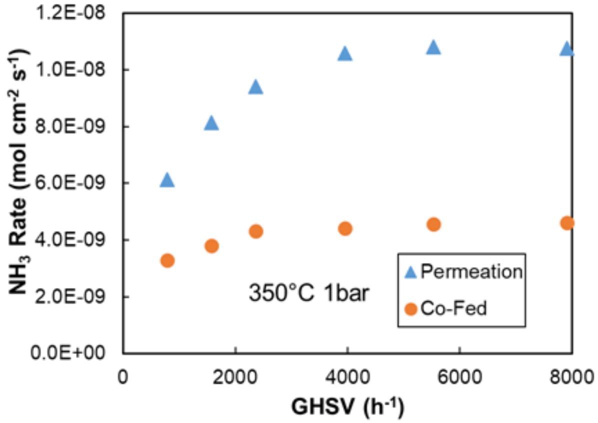
Flux > 3 x 10^{-3} mol/m^2*s

>150 hrs no degradation

Reduced T = 350°C







CHANGING WHAT'S POSSIBLE

Colin Wolden, Colorado School of Mines
Co-PIs: J. Doug Way, Jason Ganley

REFUEL

16 Project Teams • 3 Technology Areas

Portfolio – technology matrix for Category 2

Hydrogen generation (2a)

	Cracking reactor	Electrochemical cell
Mechanical compression	Rensselaer; BETTERGY Clean Energy for Better Life™	
Electrochemical compression		

Conversion to electricity in fuel cell (2b)

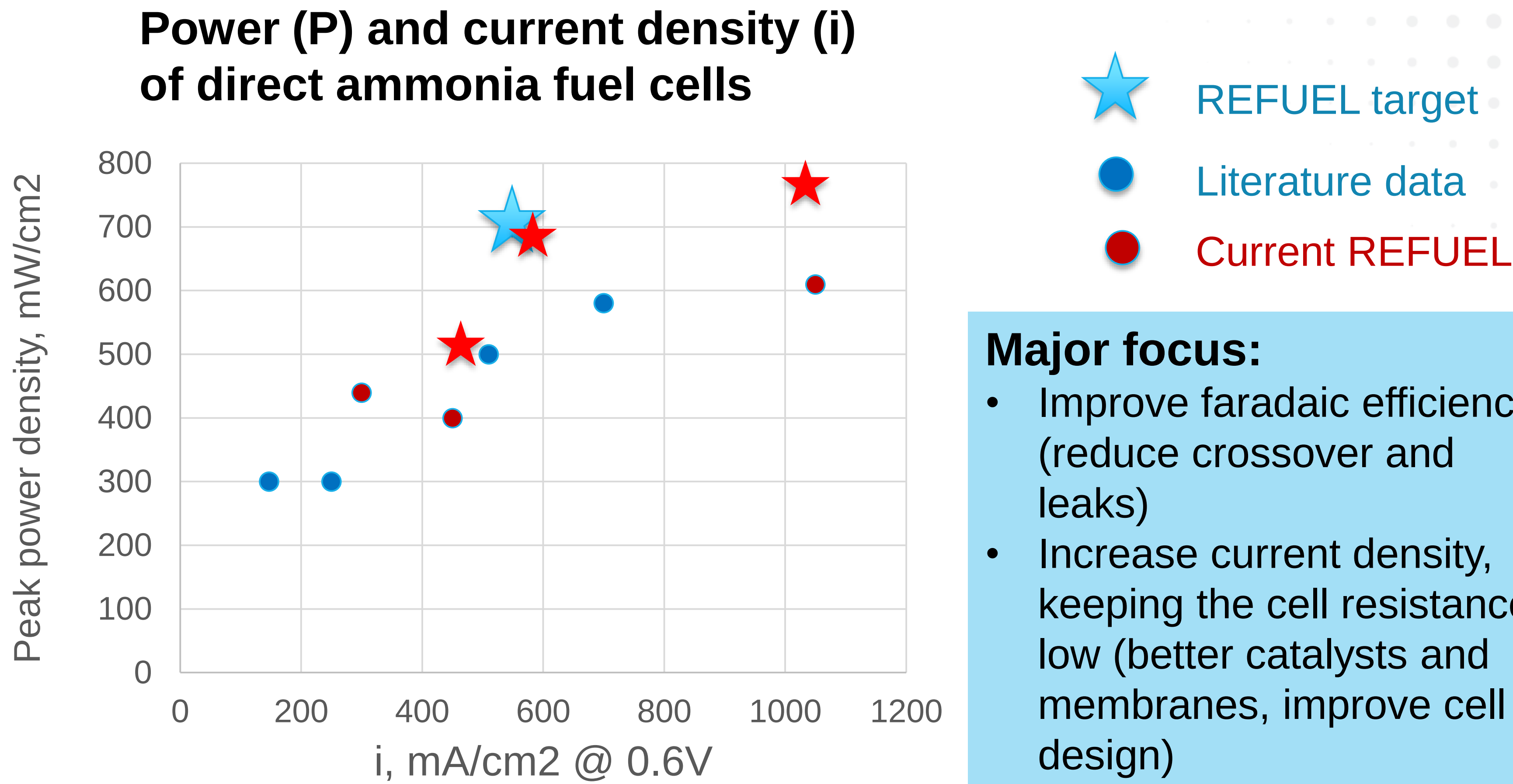
	PEM	AEM	SOFC
Low temperature (<120 C)		University of Delaware	
High temperature (>250 C)	FuelCell Energy		Chemtronergy

Ammonia

ROH

Seedling

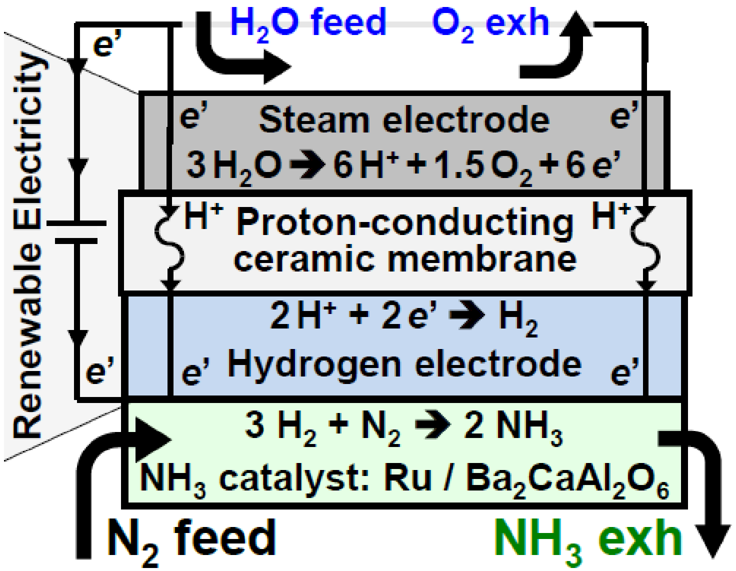
REFUEL program status: NH_3 fuel cells

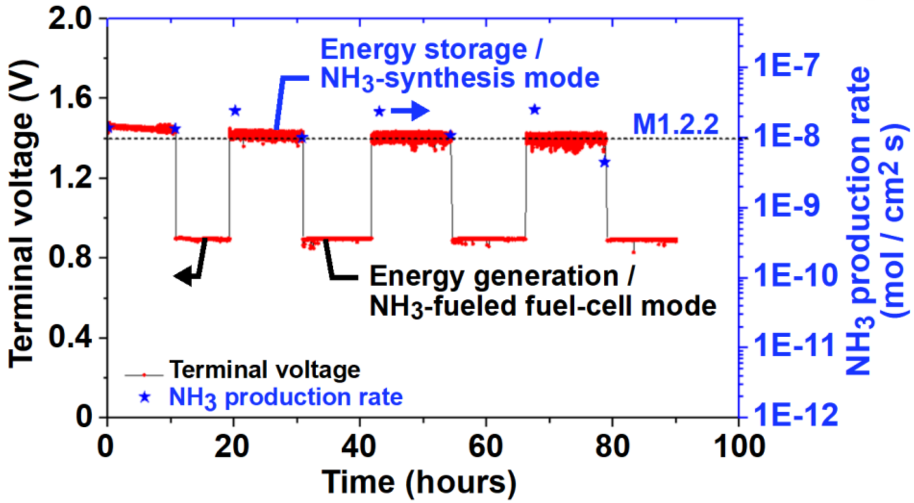


Major focus:

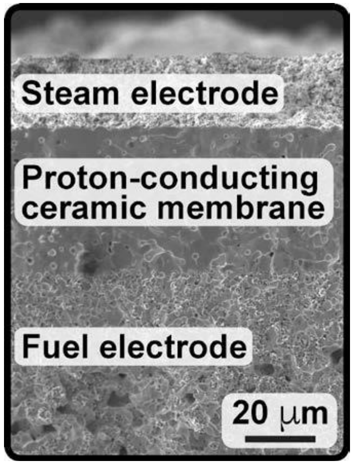
- Improve faradaic efficiency (reduce crossover and leaks)
- Increase current density, keeping the cell resistance low (better catalysts and membranes, improve cell design)
- Cell durability and scale up

Protonic Ceramics for Energy Storage and Electricity Generation with Ammonia





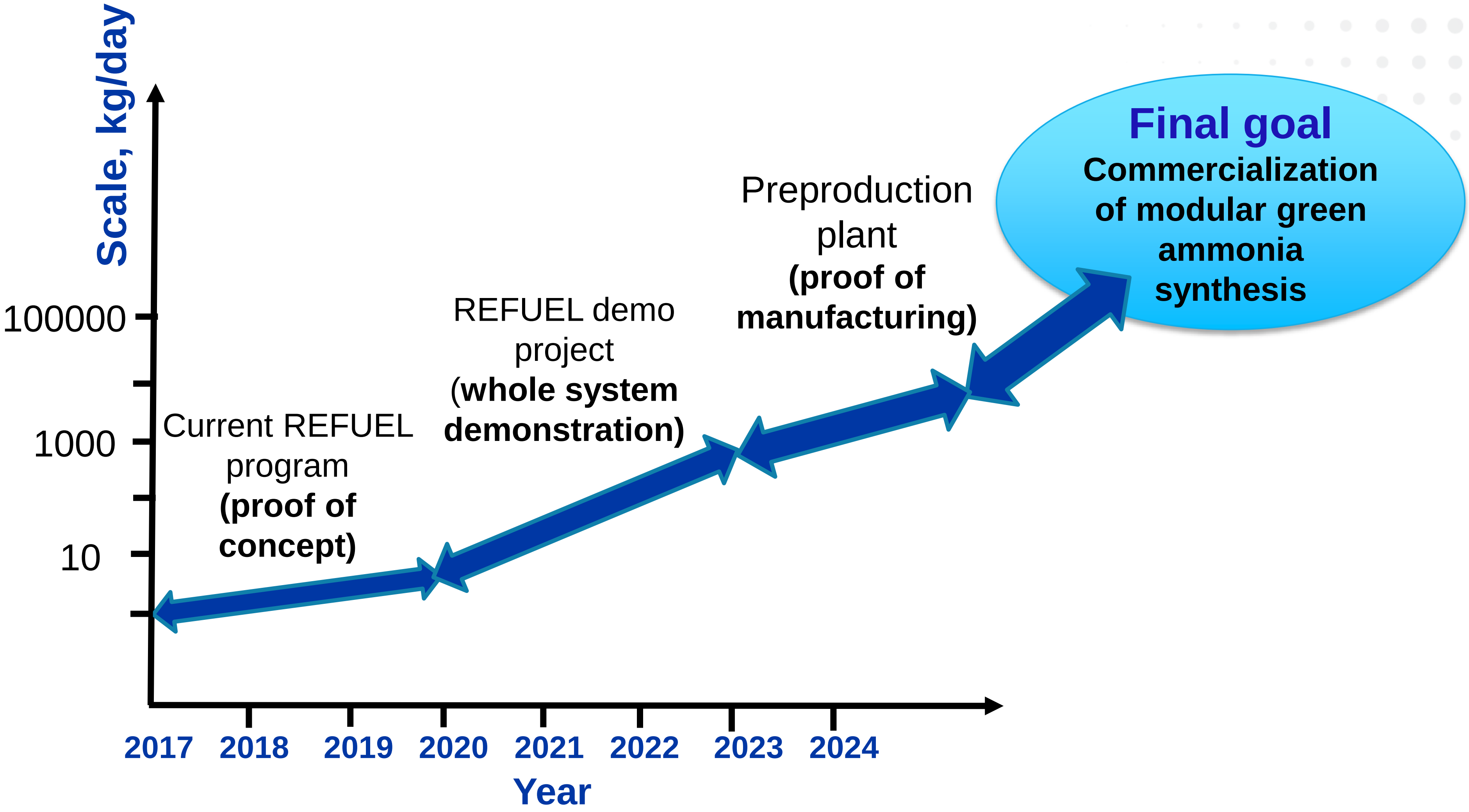
- Reached 1 x 10^{-7} mol NH_3/cm^2 s
- 2 bar gage pressure, 600 ºC
- Steam electrolysis at 0.5 A/cm^2 produces H_2
- H_2 co-fed (recycle) with N_2 to fuel electrode
- Near 35% of equilibrium NH_3-synthesis rate
- 300 mA/cm^2 in fuel cell mode
- Reasonable degradation rate



fuelcellenergy

H. Ghezel-Ayagh, FuelCell Energy, Inc.
N.P. Sullivan, R.P. O'Hayre, R.J. Kee, Colorado School of Mines

Technology development path



REFUEL demo project

Objective:

- Build a modular, flexible plant for testing ammonia synthesis technologies under reduced pressure and temperature
- Demonstrate applicability of improved Haber-Bosch technologies developed under REFUEL program for green ammonia production using intermittent energy at commercial scale
- Collect real life data for engineering of a preproduction ammonia plant
- Prepare technology for licensing

Deliverable:

- Containerized mini-plant for green ammonia production at the rate 1 metric ton per day
- Verified performance and cost model suitable for building of larger plants

REFUEL demo project: roles and responsibilities

- **Core technology developer(s)**
  - catalyst development
  - ammonia separation
  - reactor design
- **Integrator (prime)**
  - engineer, build and commission the containerized plant
- **Demonstrator (site owner)**
  - access to renewable electricity, permits, plant operation, ammonia use
- **Vendor/suppliers**
  - water electrolyzer
  - air separation unit
  - pumps, valves, tubes, controls, etc.
- **Backers**
  - provide financial support
- **ARPA-E**: active project management

REFUEL demo project: timeline

- **Phase I – design (12 months)**
  - technologies refinement
  - mini plant design
  - P&ID
  - plant TEA
  - selection and ordering of components and parts
- **Phase II – constructing (12-15 months)**
  - finish development and lock technologies
  - test major components
  - construct the plant
  - commission the plant
  - prepare the test site
- **Phase III – field testing (9-12 months)**
  - deliver the plant and connect it to the infrastructure
  - run tests in real time
  - collect data and refine the cost/performance model
  - use ammonia (optional)

Flexible modular plant by Bayer
https://www.process-worldwide.com

Conclusions

- Improved Haber-Bosch process combined with water electrolysis (HB+WE) is a short term solution for generation of “green” ammonia from renewables at matching scale
- Major focus on reducing the NH_3 synthesis pressure and temperature and operation with intermittent energy supply
- HB+WE is close to demonstration stage
- Substantial progress in electrochemical ammonia synthesis (production rate **10^{-7} mol-NH_3/$cm^2 \cdot s$ vs** 10^{-8} - 10^{-9} lit) but still far away from commercialization
- Performance milestones for ammonia fuel cells and hydrogen generation from ammonia met, durability and manufacturing are the next targets

Research needs and path forward

- Development of better catalysts and electrocatalysts
- Development of technologies for ammonia separation at low pressures (absorbents, membranes)
- **Demonstration of the whole system in the real world environment (demo project planned)**
- Combination of electrochemical and chemical pathways to compensate for low faradaic efficiency
- Suppressing water activity in electrochemical pathway (concentration, chemical bonding, delivery)

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Thank you!