CHANGING WHAT'S POSSIBLE

FUTURE OF AMMONIA PRODUCTION: IMPROVEMENT OF HABER-BOSCH PROCESS OR ELECTROCHEMICAL SYNTHESIS?

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AIChE Annual Meeting
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U.S. DEPARTMENT OF ENERGY

Sustainable fuels as energy vector

1) Reduce transportation and storage 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

Sustainable liquid fuels

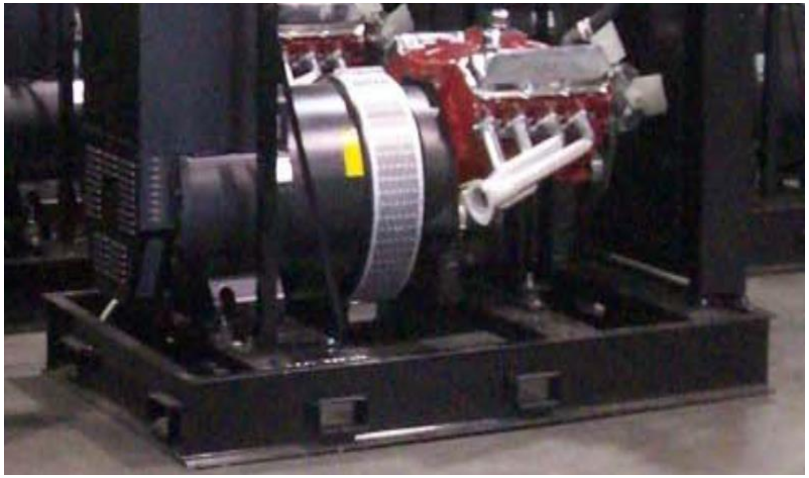
Fuel	B.p., deg C	Wt. % H	Energy density, kWh/L	E^0, V	η, %
Synthetic gasoline	69-200	16.0	**9.7**	-	-
Biodiesel	340-375	14.0	**9.2**	-	-
Methanol	64.7	12.6	4.67	1.18	96.6
Ethanol	78.4	12.0	**6.30**	1.15	97.0
Formic acid (88%)	100	3.4	2.10	1.45	105.6
Glycerol	**290**	8.7	**6.21**	1.21	**101.4**
Ammonia	-33.3	**17.8**	**4.32**	1.17	88.7
Hydrazine hydrate	114	8.1	**5.40**	**1.61**	**100.2**
Liquid hydrogen	-252.9	100	2.54	1.23	83.0
Compressed hydrogen (700 bar)	gas	100	1.55	1.23	83.0

G.Soloveichik, *Beilstein J. Nanotechnol.* **2014,** *5,* 1399

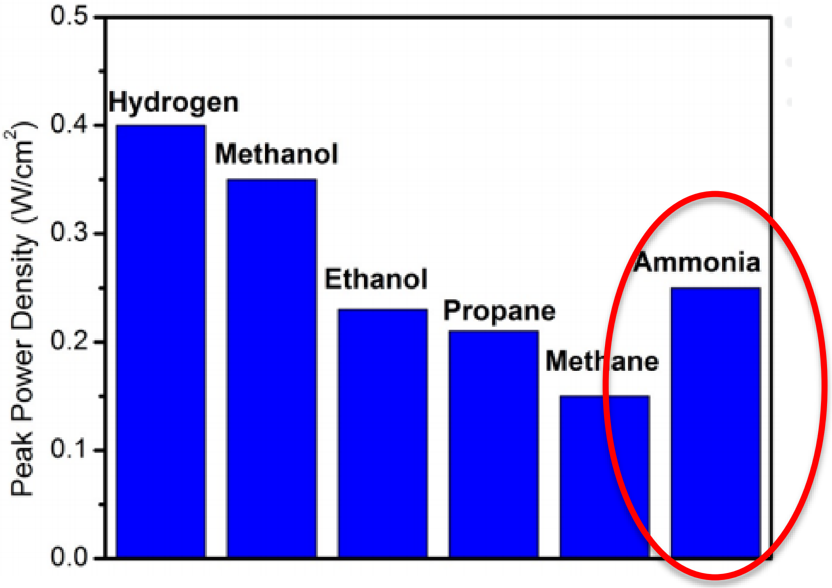
Use of ammonia for power generation

Internal combustion engines
- neat ammonia
- blends with fossil fuels
- partially reformed (cracked) NH_3

Fuel cells
- neat ammonia
- internal fuel reforming
- power density comparable with H_2 fuel



HEC-TINA 75 kVA
NH_3 Generator Set



Colorado School of Mines
Peak power density, 500 C

Technologies to be developed

Cost effective fuel synthesis

- Hydrogenation reactions (better, modular Haber-Bosch)
- One-step reactions using water as a hydrogen source

Efficient power generation from fuels

- Direct conversion to electricity
- Combustion in thermal engines
- Intermediate hydrogen formation

Electrochemical vs. thermal (catalytic) technologies

- Higher efficiency >> energy savings
- Higher selectivity >> less purification needed
- Lower temperatures and pressures >> lower BOP
- Linear scalability >> better suited for small to medium scale

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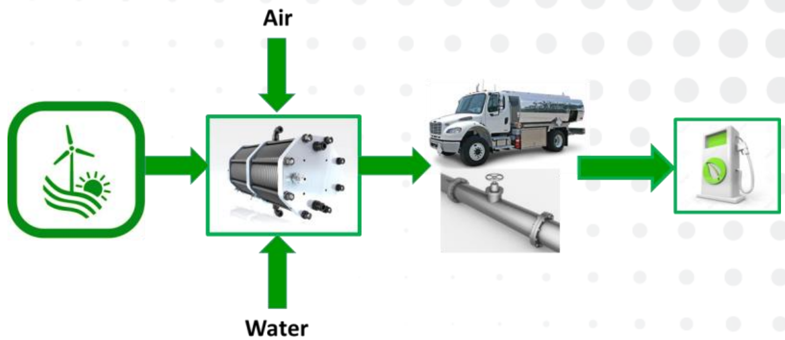
Renewable Energy to Fuels through Utilization of Energy-dense Liquids



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 .

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

16 Project Teams • 3 Technology Areas

Portfolio – technology matrix for Category 1

Thermal (catalytic) processes (1a)

	Equilibrium shift	Reactor design
Hydrogenation catalyst (e.g. Haber-Bosch)	gti	RTI INTERNATIONAL
Physical effects (e.g. plasma)		

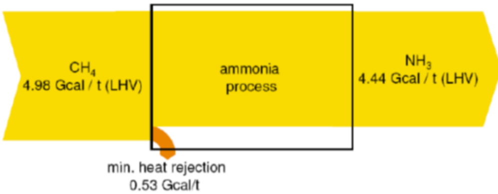
Electrochemical processes (1b)

	PEM	AEM
Low temperature (<120 C)	Sustainable Innovations; OPUS 12	WSU; GINER
High temperature (>250 C)	FuelCell Energy; CERAMATEC TOMORROW'S CERAMIC SYSTEMS	storaGENergy technologies; MoleculeWorks Efficiency for a Sustainable World

ROH

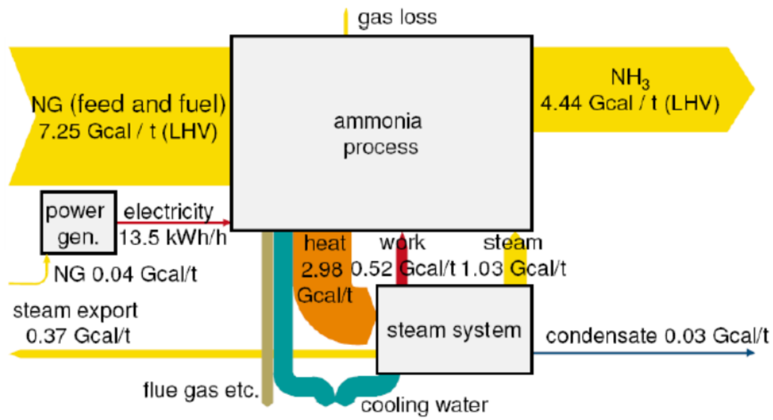
Haber-Bosch process improvement

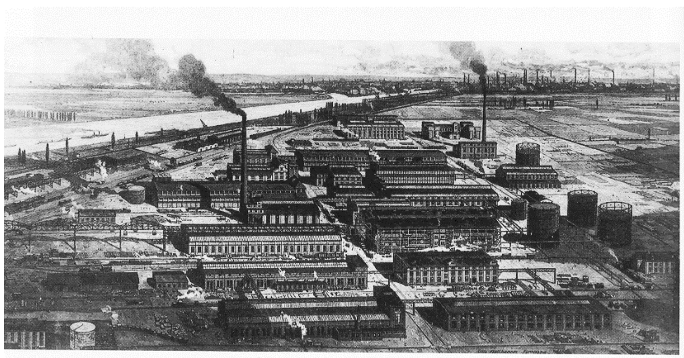
Theory



Efficiency: 61 - 66% (SMR)
54% (electrolytic H_2)

Practice





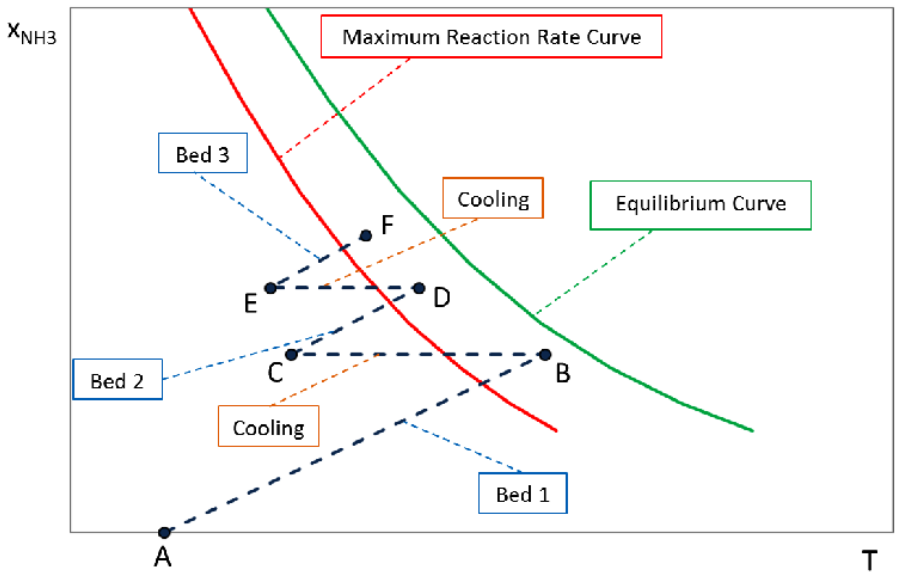
Die Ammoniakfabrik der BASF in Oppau. Gemälde von Otto Bollhagen, 1914. Ludwigshafen, Unternehmensarchiv BASF

First NH_3 plant in Oppau, 9,000 tons/year

BASF plant in Ludwigshafen, 875,000 tons/year

- **Efficiency is still low**
- **Gigantic plant size to be economical**

Haber-Bosch process improvement



Courtesy of F. Ermanno, Casale SA

Improvement needs

Higher catalyst activity at lower temperature

- higher conversion per pass
- less power for gas circulation
- smaller equipment
- easier NH_3 condensation

Lower operational pressure

- lower energy consumption
- lower CAPEX

Alternative NH_3 product separation

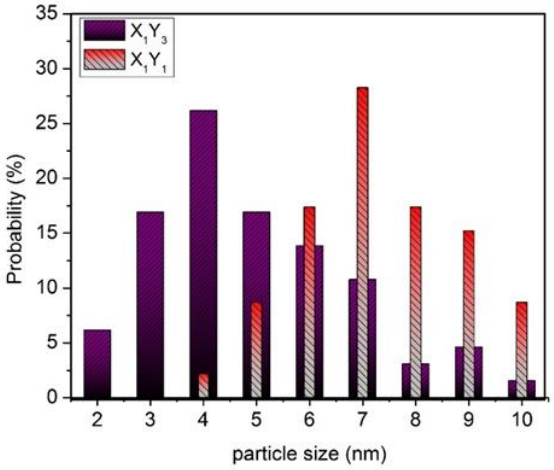
- simpler synthesis loop
- lower energy consumption

Capability to follow variable plant load

- enable renewables as energy source

Haber-Bosch process improvement

RTI International: Innovative Renewable Energy-Based Catalytic Ammonia Production (REFUEL)



Project Vision

Higher efficiency solid electrolyte membrane based process to synthesize carbon free ammonia for long term energy storage

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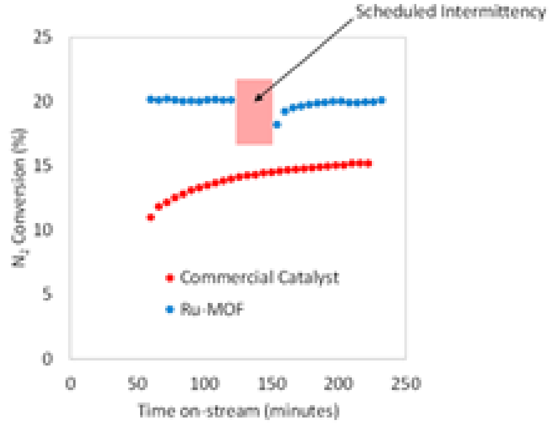
Innovation

- Development of a breakthrough metal organic framework-based ammonia synthesis catalyst enabling operations at lower temperatures and pressures
- Novel ammonia synthesis loop control under intermittent loads
- Optimized and scalable advanced low-cost technology for air separation for the production of high-purity nitrogen



Data courtesy J. Carpenter, RTI International

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RTI INTERNATIONAL

Haber-Bosch process improvement

University of Minnesota: Wind to Ammonia (REFUEL)

Project Vision

Lower pressure ammonia synthesis for distributed generation

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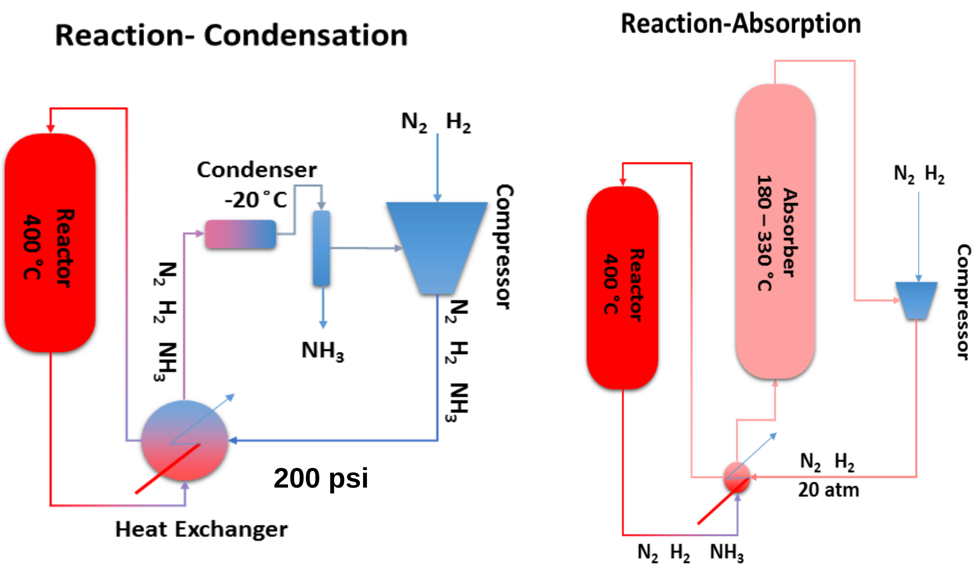
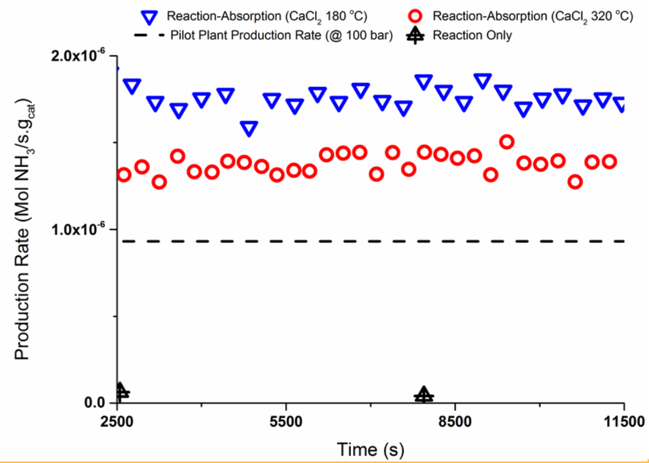
Innovation

- High temperature ammonia separation using solid adsorbents at lower pressure
- Minimal compression & heat exchange





Data courtesy A. McCormick, University of Minnesota

Higher production rate with reaction-absorption

Electrochemical synthesis of ammonia

$$H_2O \rightarrow H_2 + 0.5O_2 \qquad E^0 = 1.23V$$

$$3H_2 + N_2 \rightarrow 2NH_3 \qquad E^0 = 0.08V$$

$$3H_2O + N_2 \rightarrow 2NH_3 + 1.5O_2 \qquad E^0 = 1.14V$$

- **Reaction of electrolytic hydrogen with nitrogen**
  - two step process
  - proton conducting membranes
- **Direct electrochemical reaction of nitrogen with water**
  - both HT proton and hydroxyl conducting membranes may be used
  - hydrogen evolution side reaction
  - high overvoltage due to oxygen evolution reaction
  - multistep processes
- **Electrochemical/chemical path via lithium nitridation**
  - lithium electrochemical production is energy demanding

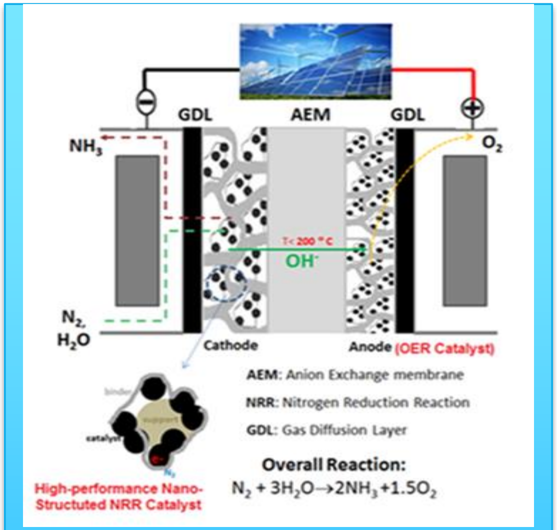
Giner: development of ammonia synthesis catalysts for AEM electrolyzer (REFUEL)

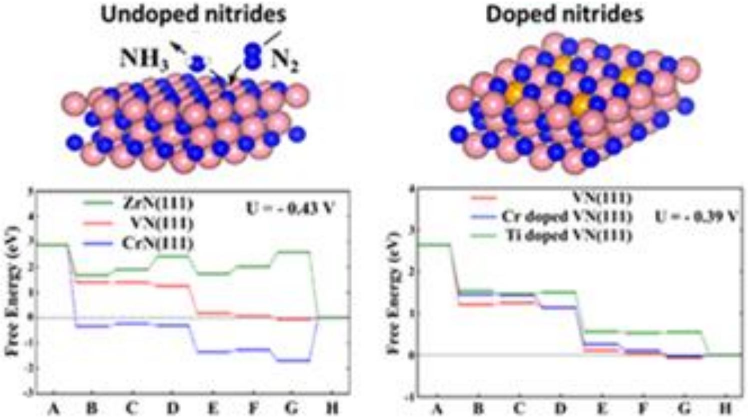
Project Vision

The proposed project aims to design and implement advanced components (e.g. catalyst and membrane) to transform the efficiency of electrochemical synthesis of ammonia (ESA) using air, water and renewable energy.

Innovation

- High-performance selective catalysts to boost ammonia synthesis while inhibiting hydrogen evolution
- **Durable high-temperature alkaline membranes (>100 ℃) to promote the ammonia production reaction**
- State-of-the-art electrolyzer cell design to maximize the ammonia production efficiency





Data courtesy H. Xu, Giner

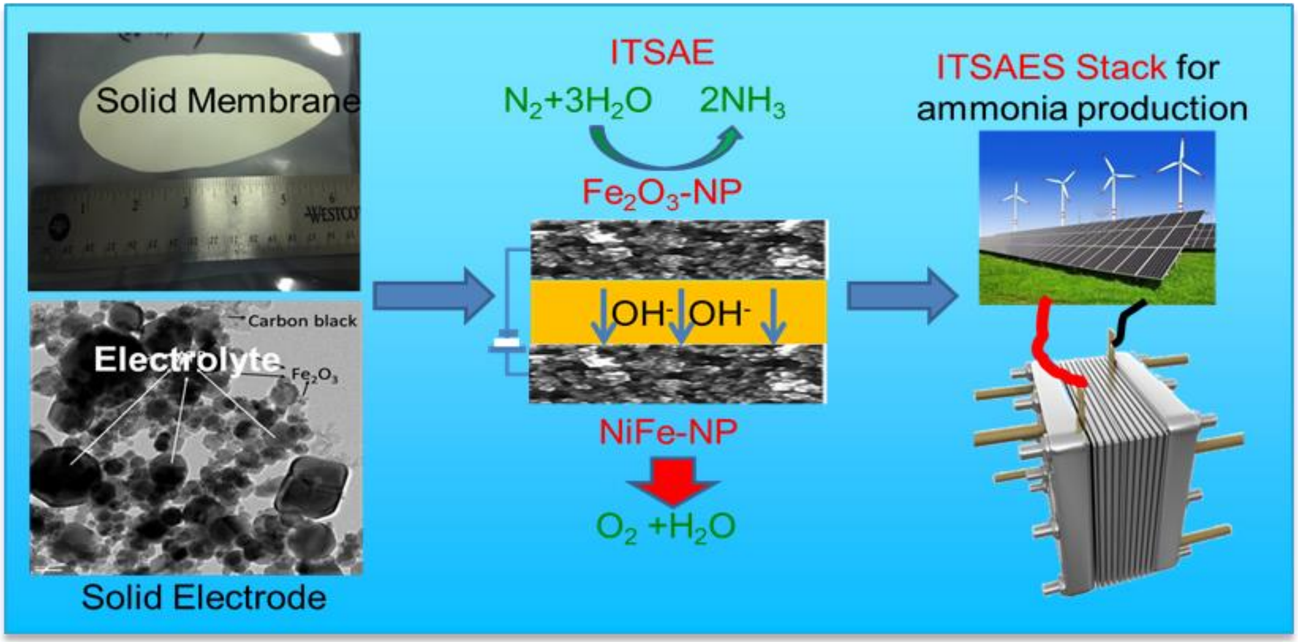
Storagenergy Technologies: development of ammonia synthesis electrocatalysts for intermediate temperature solid-state alkaline electrolyzer (REFUEL)

Project Vision

Develop an intermediate temperature (100-300oC) solid-state alkaline electrolyzer for high-rate ammonia production from air and steam electrolysis

Innovation

The ITSAE integrates **cost-effective and highly OH-conducting membrane,** novel nanostructured Fe2O3-based nitrogen reduction reaction (NRR) cathode catalyst, and amorphous noble metal free NiFeOx nanoparticle (2-4 nm) oxygen evolution reaction (OER) anode catalyst.



Data courtesy J. Bi, Storagenergy Technologies Inc.

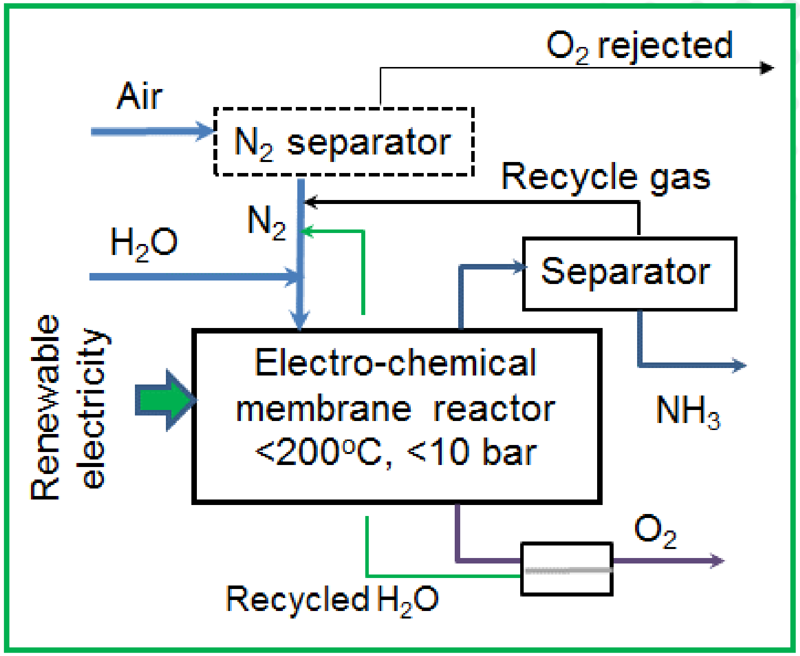
Molecule Works Inc.: nanocatalysts for electrochemical membrane reactor for ammonia synthesis (REFUEL)

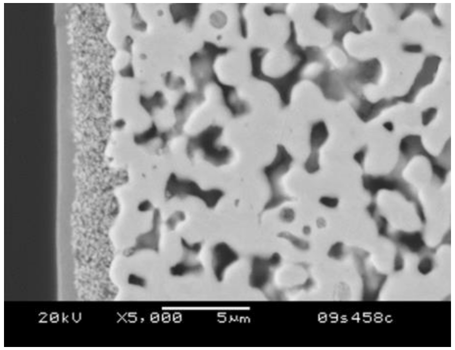
Project Vision

Developing compact modular reactor technologies for efficient ammonia production from air and water with renewable electrical power

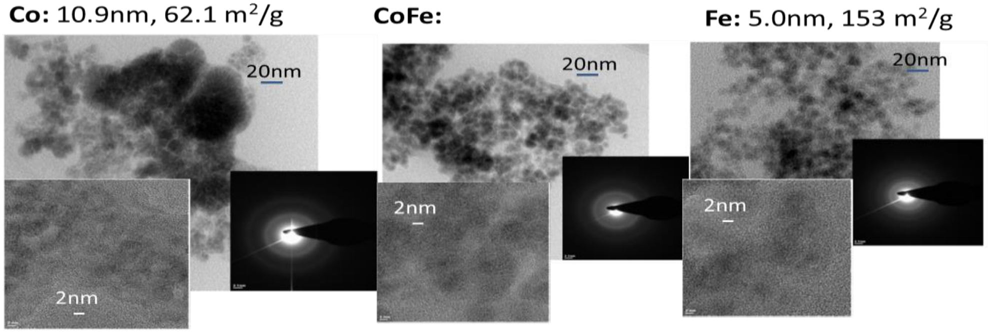
Innovation

- **KOH electrolyte immobilized in porous ceramic membrane electrode assembly (MEA) for solid-state cell operation from 50-180oC**
- Nano-catalyst incorporated into porous metal sheet cathode of high surface area



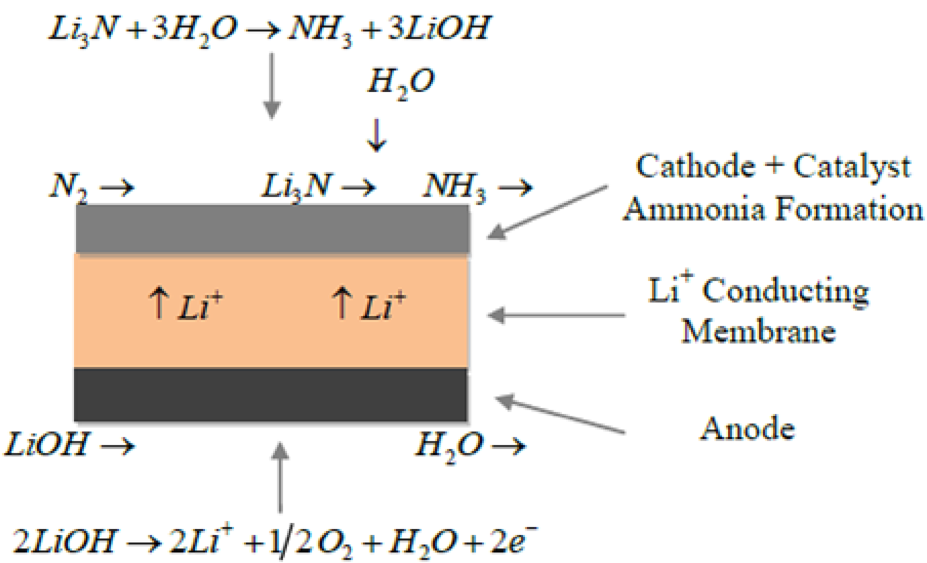


Meso-porous ceramic coating as separator



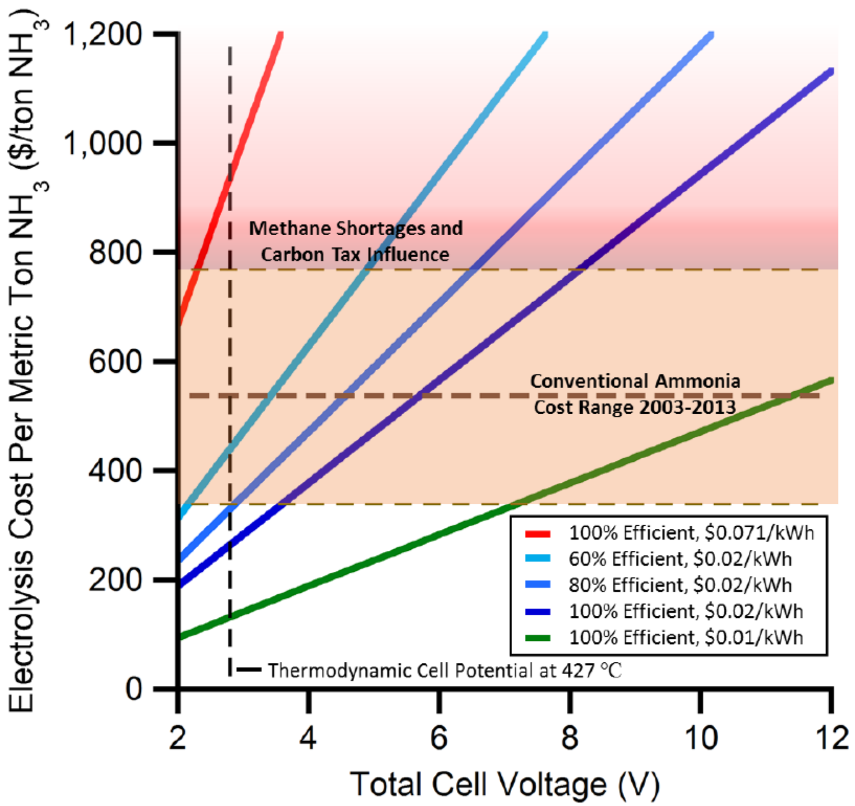
Data courtesy W. Liu, Molecule Works Inc.

Electrochemical/chemical pathway via N_2 activation by metal lithium



Data courtesy S. Balagopal, Ceramatec

Under current conditions this technology can compete with Haber-Bosch process at low electricity cost (<$0.02/kWh)



McEnaney J. et al. *Energy Environ. Sci.* 2017. **10**, 1610.

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Electrochemical/chemical pathway via N_2 activation by metal lithium

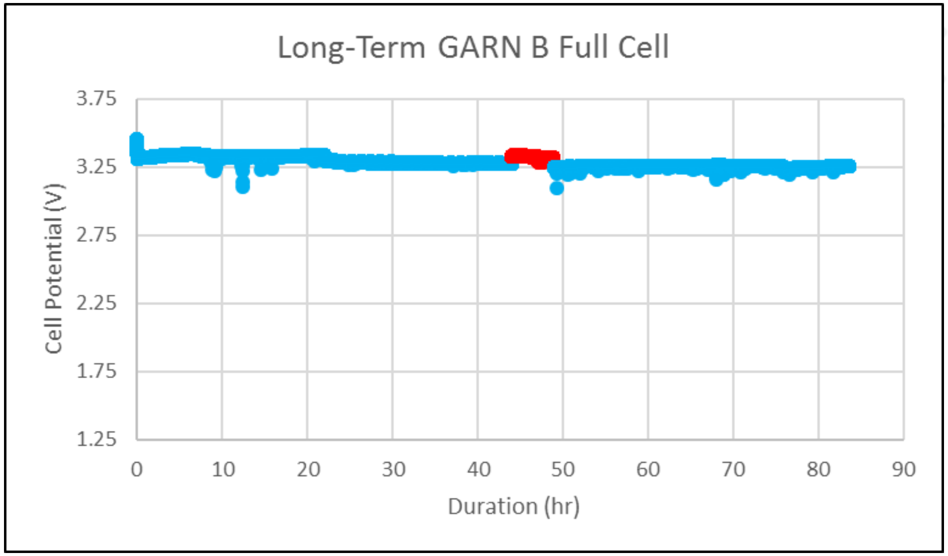
Ceramatec: Electrochemical Ammonia Synthesis for Grid Scale Energy Storage (OPEN 2015)

Project Vision

Enabling the storage of renewable energy as ammonia fuel by combining the development of a novel ammonia synthesis catalyst with process design focused on the variability in the renewable energy input.

Innovation

- Synthesis of NH_3 using electrochemical-chemical pathway at moderate temperatures (< 350°C) and pressures (< 0.5 atm.).
- **Generate ammonia via reaction of Li_3N and water at ambient pressure and temperature**
- Li+ membrane process using highly conductive roprietary membrane developed at Ceramatec.



Li cell operated-23.5mAh
NH_3 synthesis @ $1.31\text{x}10^{-8}$ mol $NH_3/cm^2/s$ @ 76% conversion efficiency demonstrated.

Data courtesy S. Balagopal, Ceramatec

Conclusions

Haber-Bosch improvement:

- Low hanging fruit
- Low temperature, low cost catalyst
- Ammonia removal to shift equilibrium

Electrochemical ammonia synthesis:

- Potentially lower energy consumption
- Hydrogen evolution side reaction
- Current density improvement needed

Common needs:

- Efficient, low cost, modular air separation

Thank you!