CHANGING WHAT'S POSSIBLE

Ammonia for Energy Storage and Delivery

Grigorii Soloveichik,
Program Director

NH3 Fuel Conference 2016
September 19, 2016

U.S. DEPARTMENT OF ENERGY

Outline

- ARPA-E mission and work
- Needs for zero-carbon fuels
- Ammonia as a fuel
- Ammonia synthesis
- Ammonia for energy transportation
- Ammonia as energy storage media
- ARPA-E REFUEL program
- Conclusions

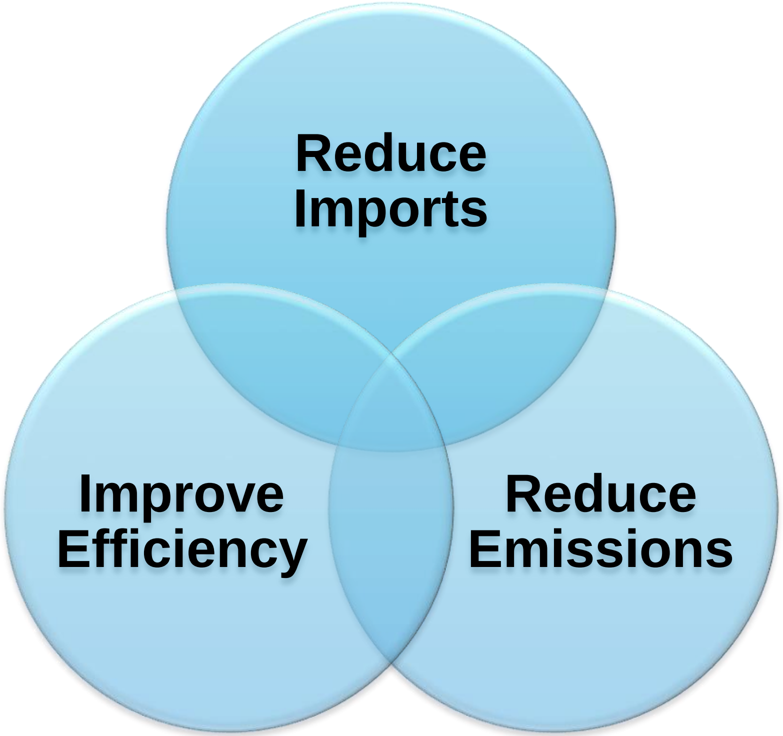
CHANGING WHAT'S POSSIBLE

ARPA-E Mission

Catalyze and support the development of transformational, high-impact energy technologies

Ensure America's

- National Security
- Economic Security
- Energy Security
- Technological Lead



www.arpa-e.energy.gov

What Makes an ARPA-E Project?

IMPACT

- High impact on ARPA-E mission areas
- Credible path to market
- Large commercial application

TRANSFORM

- Challenges what is possible
- Disrupts existing learning curves
- Leaps beyond today's technologies

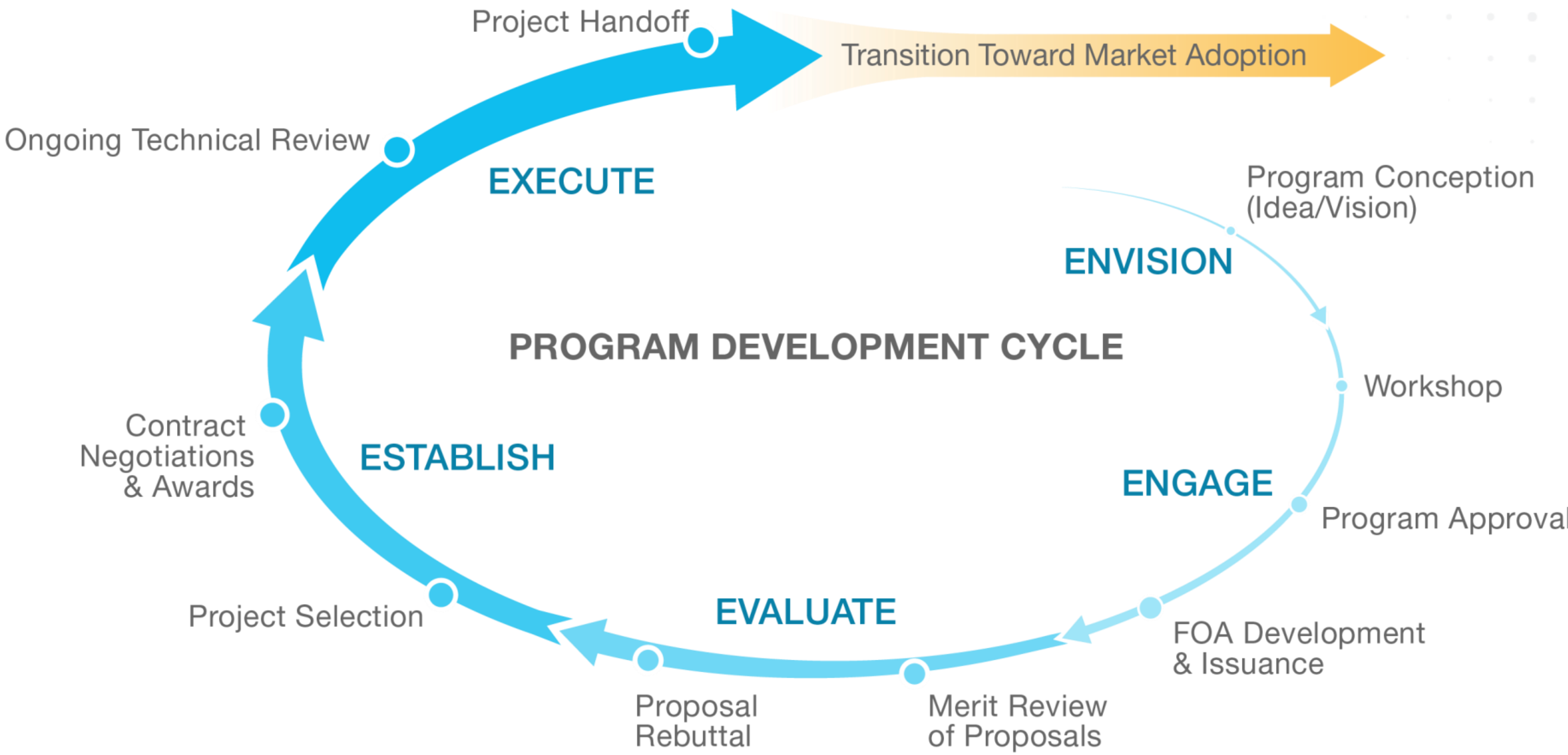
BRIDGE

- Translates science into breakthrough technology
- Not researched or funded elsewhere
- Catalyzes new interest and investment

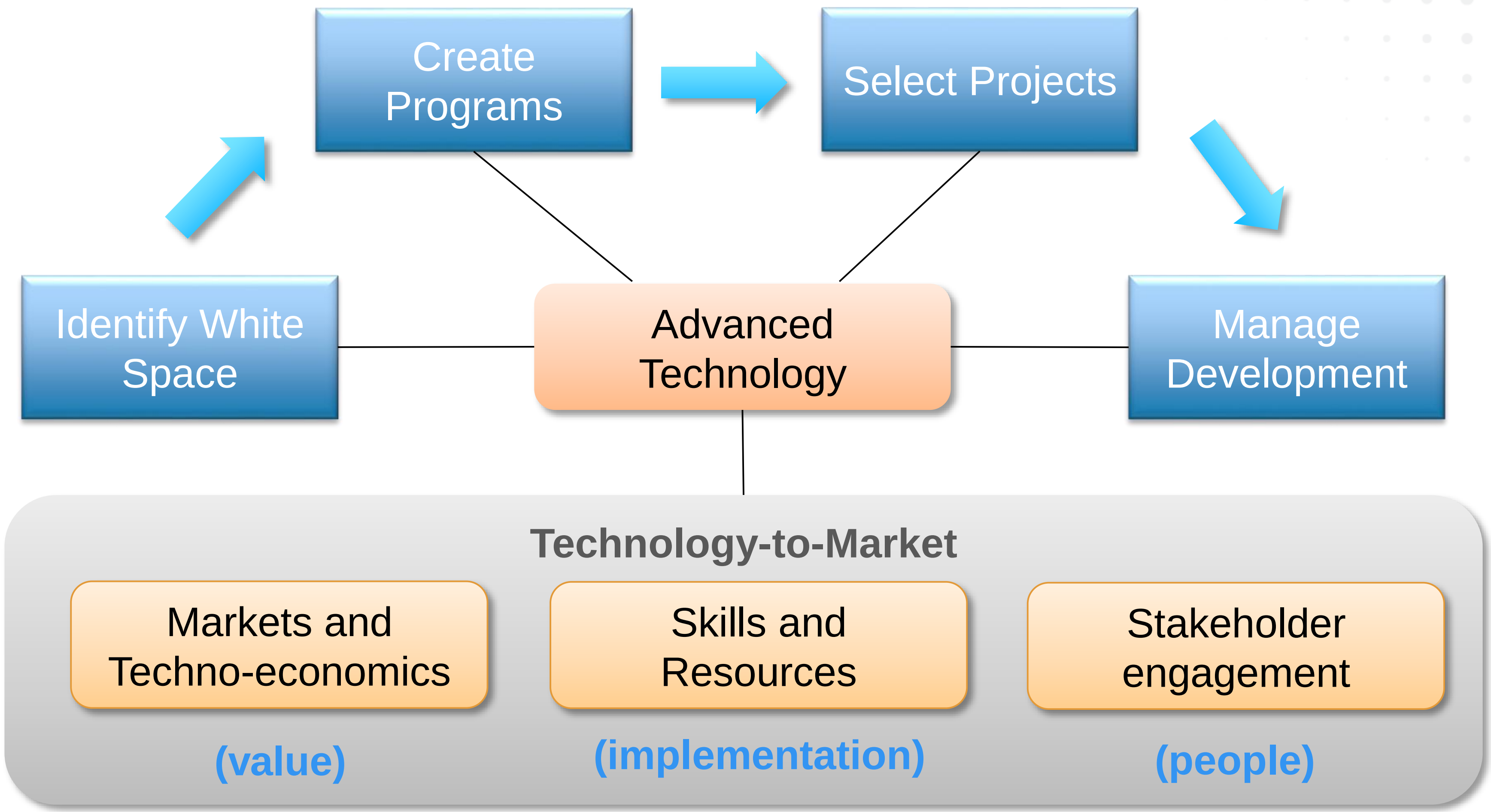
TEAM

- Comprised of best-in-class people
- Cross-disciplinary skill sets
- Translation oriented

Technology Acceleration Model



Changing the Model



Measuring ARPA-E's Success

MOVING TECHNOLOGY TOWARD MARKET

- Partnerships with other government agencies
  - 16 government projects
- New company formation
  - 24 new companies formed
- Established company relationships
- New communities
- Products in the marketplace
  - 4 products with commercial sales
- Follow-on Funding
  - 22 projects have attracted more than $625 million form the private sector after ARPA-E's investment of approximately $95 million

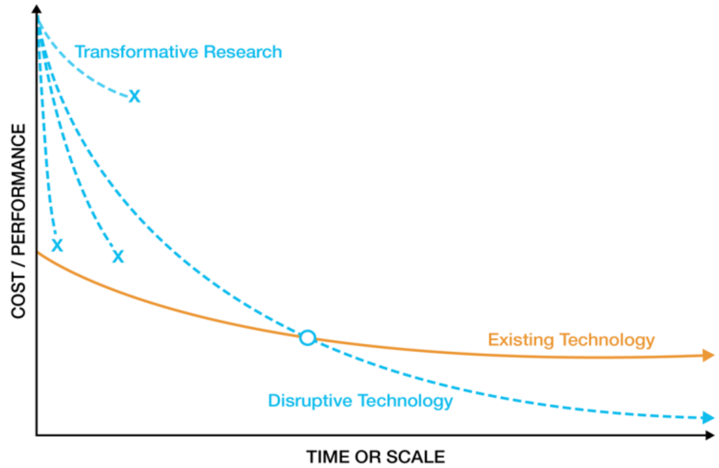
BREAKTHROUGH ACHIEVEMENTS

- Technology breakthroughs
- Patents
- Publications

OPERATIONAL EXCELLENCE

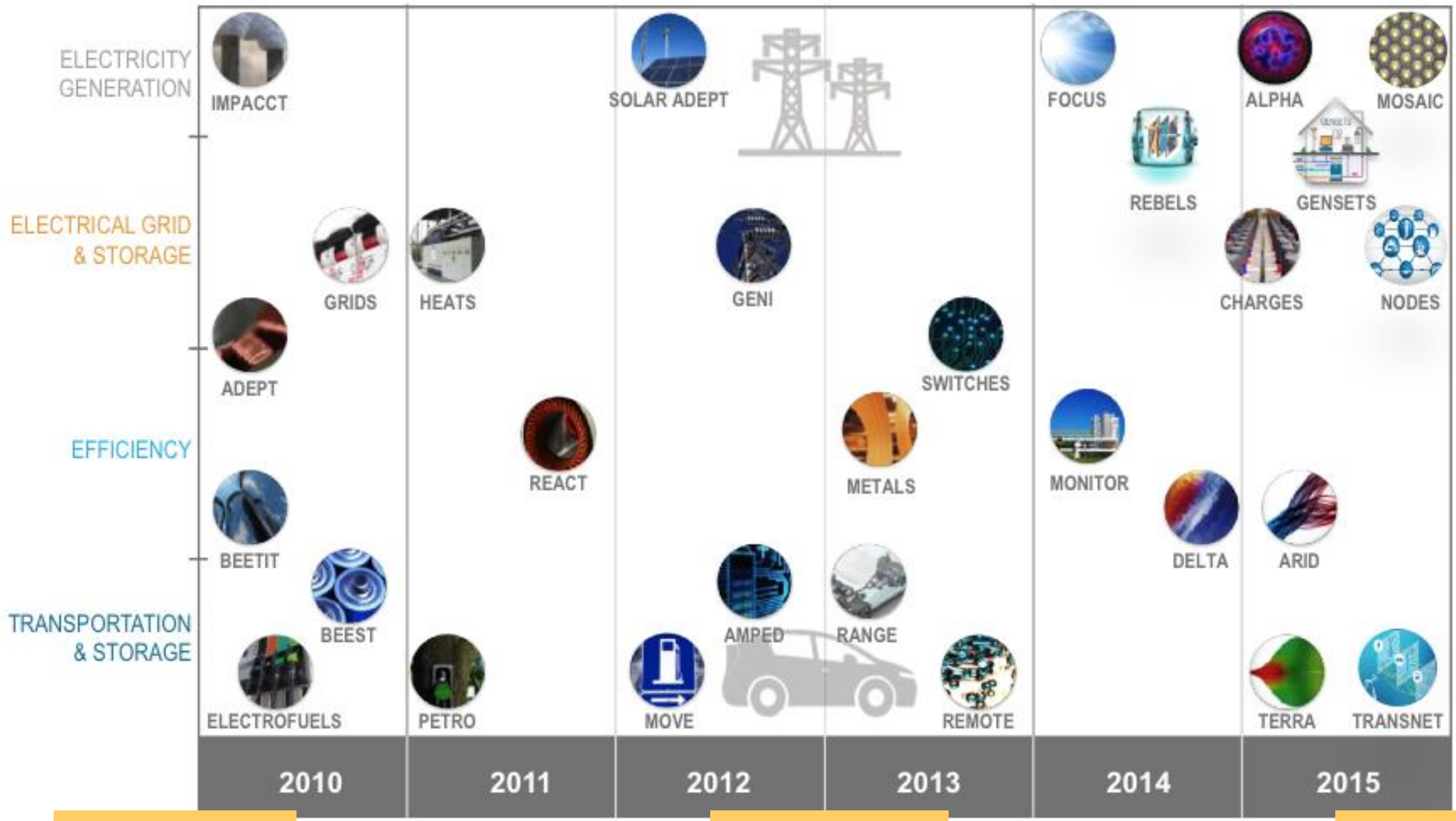
- Expedited program development and project selection
- Aggressive performance metrics

ARPA-E's Features



- **Creating new learning curves**
  - failure acceptance
- **Program driven**
  - no roadmaps
- **Innovative start-up culture**
  - combination of fresh blood and corporate memory
- **Close involvement in project planning and execution**
  - cooperative agreement
- **Technology to market focus**
  - techno-economical analysis
  - minimum value prototype deliverable
  - technology transfer

ARPA-E Programs



OPEN 2009
36 projects

OPEN 2012
66 projects

OPEN 2015
41 projects

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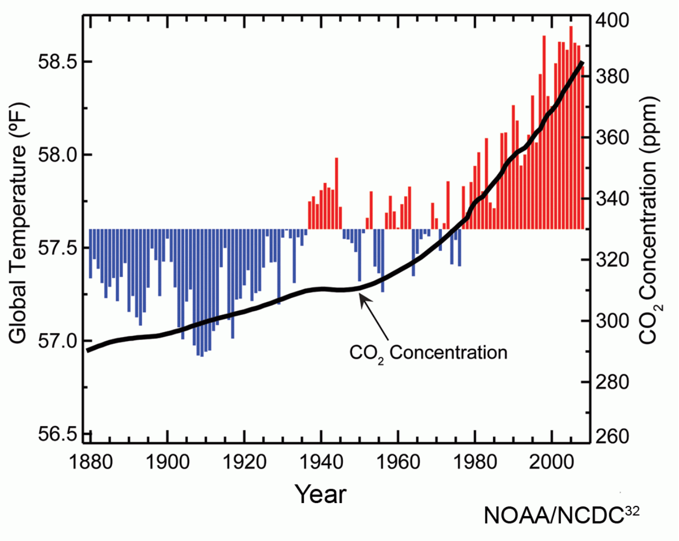
ARPA-E has funded over 400 projects across 25 focused programs and open funding solicitations

Needs for zero-carbon fuels



How to reduce GHG emissions while preserving energy and economy security

- **Partial solution: replace carbon intense fuels with natural gas or electricity**
  - wide use of natural gas indeed reduced GHG emissions but… total CO_2 emissions flattened last years
  - replacement of liquid transportation fuels with NG is not viable
  - current electricity mix does not provide much advantage using batteries in BEVs, low customer acceptance
- **Ultimate solution: replace fossil fuels with zero-emission regenerable fuels**
  - Biomass could provide liquid fuels with lower carbon emissions but… even all biomass cannot cover transportation fuel needs, water and energy intensive
  - Clean electricity from renewable sources can be used directly in batteries to power BEVs or indirectly to generate H_2 to power FCEVs
  - Intermittent nature of solar and wind energy requires bulk storage
  - Remote location of renewables requires energy transportation to user in the form of electricity, hydrogen or liquid fuels

Ammonia is promising media for energy storage and delivery

Main parameters of potential liquid fuels

LOHC couple	B.p., deg C	Wt. % H	Energy density, kWh/L	E^0, V	η, %
Synthetic gasoline		16.0	**9.7**	-	-
Biodiesel		14.0	**9.2**	-	-
Methanol		12.6	4.67	1.18	96.6
Ethanol		12.0	**6.30**	1.15	97.0
Formic acid (88%)		3.4	2.10	1.45	105.6
Ammonia	-33	**17.8**	**4.32**	1.17	88.7
Hydrazine hydrate		8.1	**5.40**	**1.61**	**100.2**
Liquid hydrogen		100	2.54	1.23	83.0

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

Ammonia as a fuel

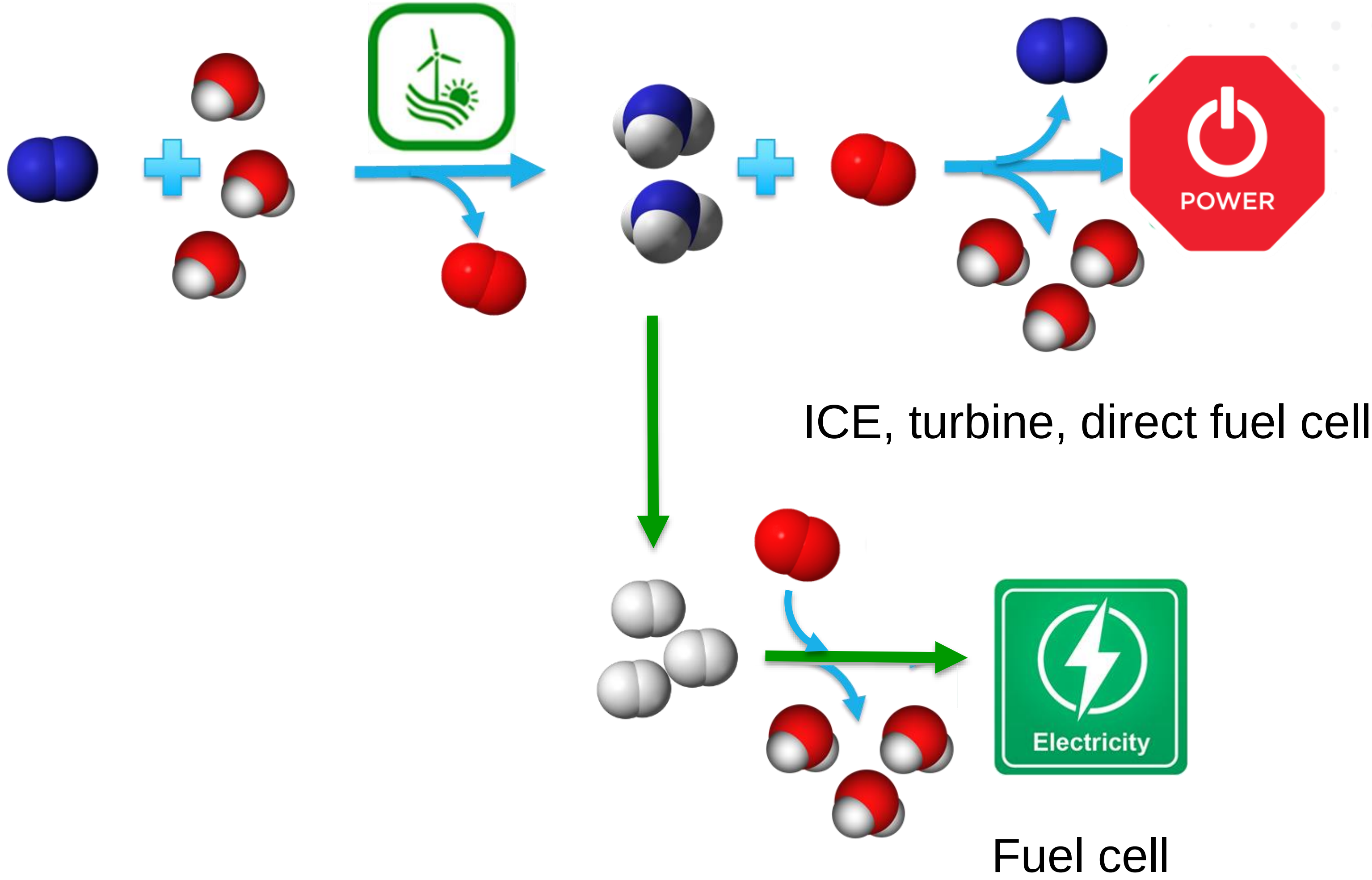
Ammonia NH_3 facts

- Properties: b.p. -33 C, density 0.73 g/cm^3,
  stored as liquid at 150 psi
  - 17,75% H, 121 kg H/m^3

- Synthesis: reaction of N_2 and H_2 under high pressure and temperature (Haber-Bosch process)
- World production 150MM tons
  - current cost about $0.5/L
- Octane number 120

- Blends with gasoline and biofuels (up to 70%)
  - mixtures preserve performance in ICE (torque)
  - proportional drop in CO_2 emission
- Partial cracking improves combustion
- **Proven, acceptable safety history for over 75 years**
  - inhalation hazard, must be handled professionally
- **Energy density 4.3 kWh/L**

Ammonia fuel cycle



Ammonia as internal combustion fuel

Norsk Hydro, Norway, 1933

Belgium, 1943

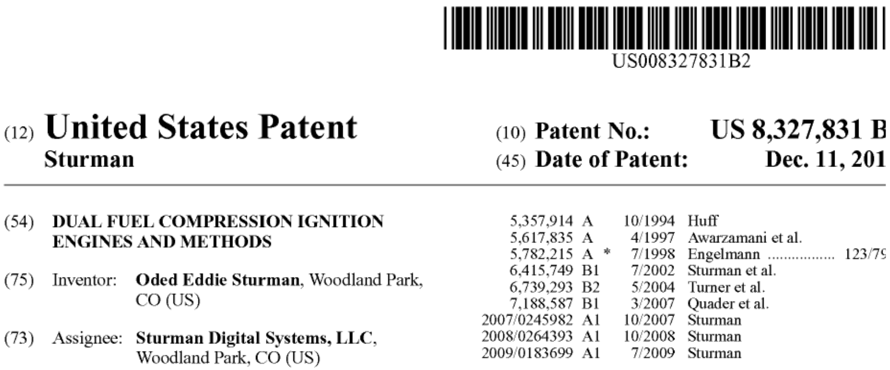
HEC-TINA 75 kVA
NH_3 Generator Set

2013 Marangoni Toyota GT86 Eco Explorer, 111 mile zero emission per tank (7.9 gal NH_3)

2013 AmVeh x250, South Korea runs on 70%NH_3 +30% gasoline

Space Propulsion Group (Palo Alto, CA) – turbines
Sturman Industries (Woodland Park, CO) – camless ICE
Toyota (Japan) – cars
Korean Institute for Energy Research (Korea) – cars -
HEC-TINA (Greeneville, TN) – gensets
AIST (Japan) – gas turbine (bifuel)

Using ammonia as a fuel


US008327831B2

(12) United States Patent
Sturman

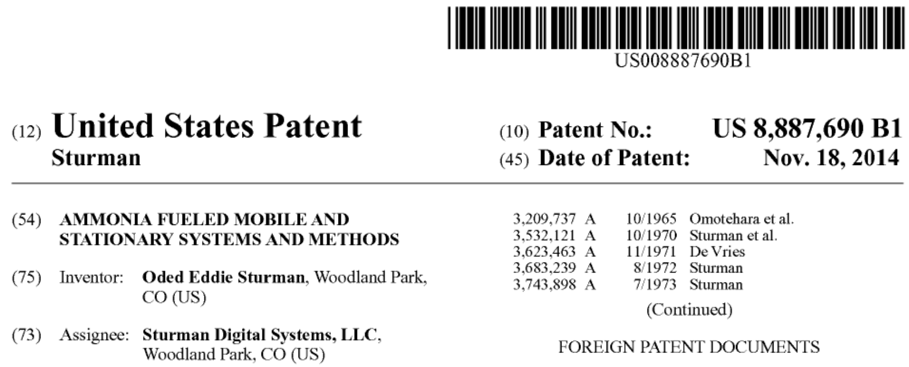
(10) Patent No.: US 8,327,831 B
(45) Date of Patent: Dec. 11, 201

(54) DUAL FUEL COMPRESSION IGNITION ENGINES AND METHODS

(75) Inventor: Oded Eddie Sturman, Woodland Park, CO (US)

(73) Assignee: Sturman Digital Systems, LLC, Woodland Park, CO (US)

5,357,914	A	10/1994	Huff
5,617,835	A	4/1997	Awarzamani et al.
5,782,215	A *	7/1998	Engelmann 123/7
6,415,749	B1	7/2002	Sturman et al.
6,739,293	B2	5/2004	Turner et al.
7,188,587	B1	3/2007	Quader et al.
2007/0245982	A1	10/2007	Sturman
2008/0264393	A1	10/2008	Sturman
2009/0183699	A1	7/2009	Sturman


US008887690B1

(12) United States Patent
Sturman

(10) Patent No.: US 8,887,690 B1
(45) Date of Patent: Nov. 18, 2014

(54) AMMONIA FUELED MOBILE AND STATIONARY SYSTEMS AND METHODS

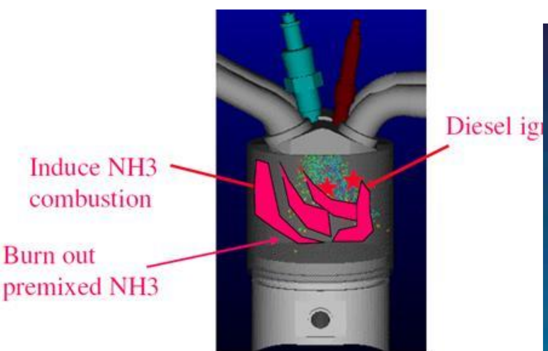
(75) Inventor: Oded Eddie Sturman, Woodland Park, CO (US)

(73) Assignee: Sturman Digital Systems, LLC, Woodland Park, CO (US)

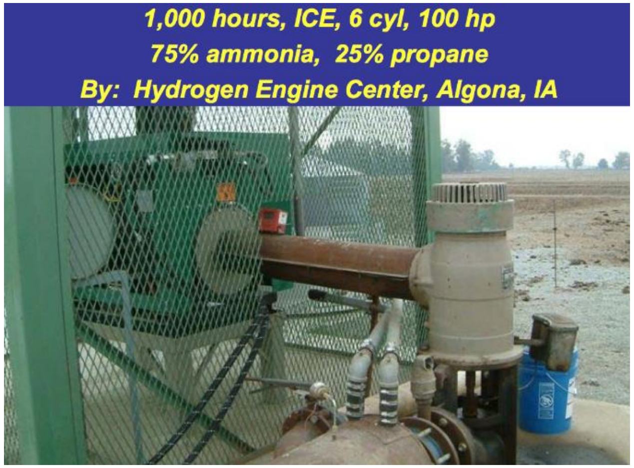
3,209,737	A	10/1965	Omotehara et al.
3,532,121	A	10/1970	Sturman et al.
3,623,463	A	11/1971	De Vries
3,683,239	A	8/1972	Sturman
3,743,898	A	7/1973	Sturman

(Continued)

FOREIGN PATENT DOCUMENTS



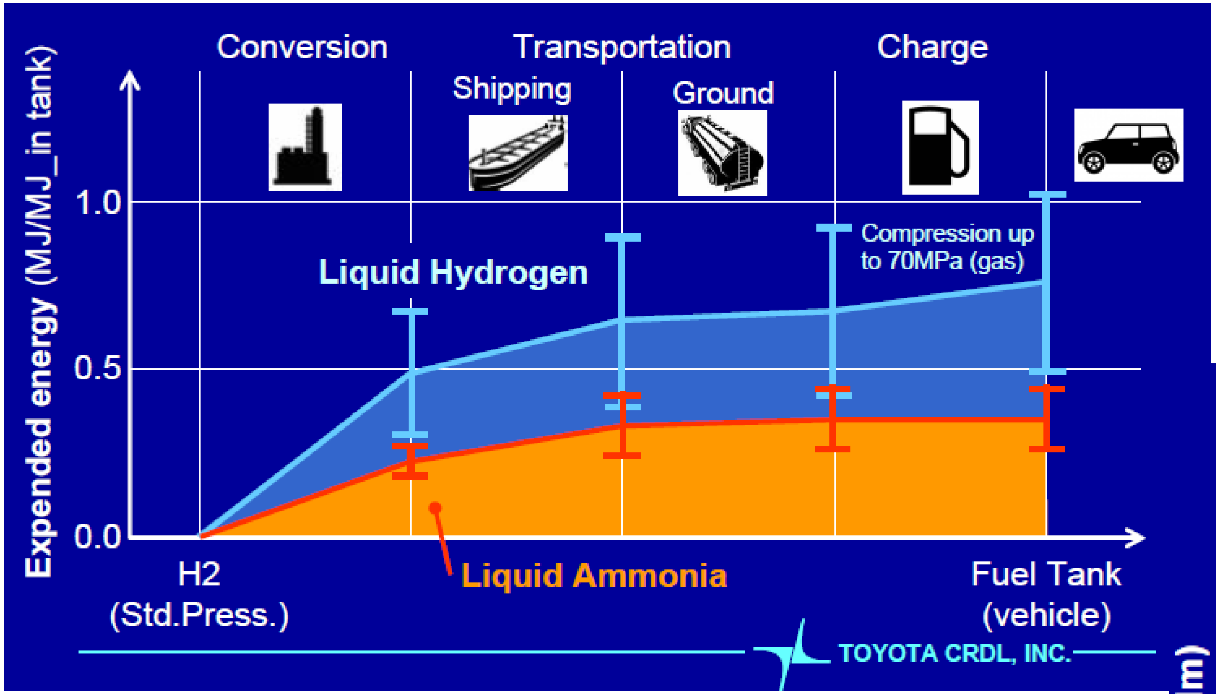
http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2008/Kong_2008.pdf



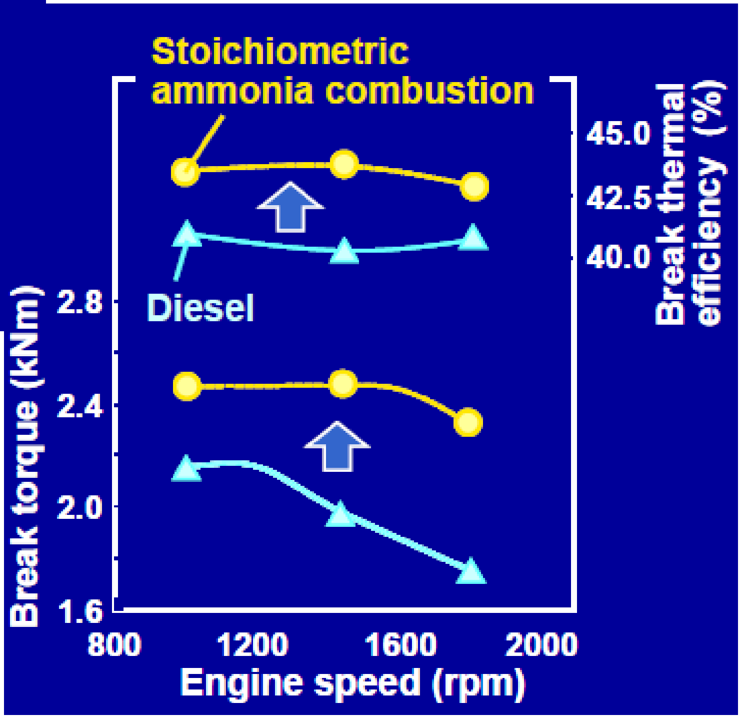
NH_3-fueled ICE operating an irrigation pump in Central Valley, CA; ~ 50% total efficiency

Sturman Industries,
Apollo Energy Systems
Iowa State University
Southwest Research Institute

Use of ammonia fuel in ICEs

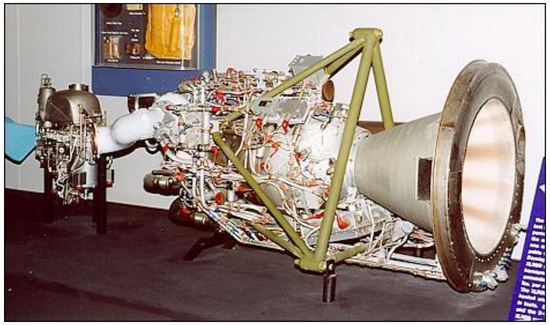


Toyota Central R&D Labs. Inc.



13L 6 cylinder engine test

Ammonia as rocket fuel



XLR99 NH_3 powered engine
500,000 hp

Ammonia powered X-15 rocket plane

- North American X-15 rocket plane (1955 – 1969)
  - 199 missions (2 space missions)
  - held speed (6.7 Mach) and altitude (108 km) records for airplanes
- Energomash (Russia) develops a new rocket engine working on a mixture of acetylene and ammonia (20 times cheaper than hydrogen) Source: Izvestia

Ammonia NH_3

Safety/environmental

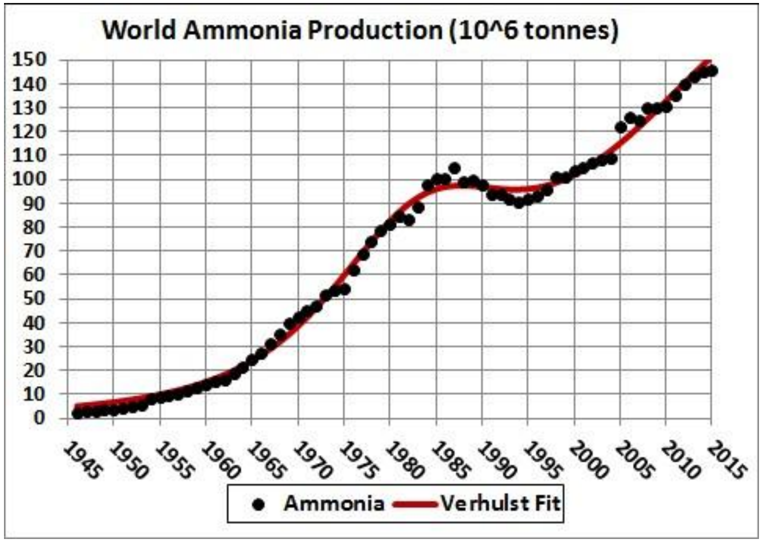
- Inhalation hazard, so must be handled carefully
- Millions of tons are stored, transported, and handled every year
- Proven, acceptable safety history for over 75 years
- Not corrosive
- Not explosive nor highly flammable
- Can be stored at moderate pressures
- Safer than gasoline or propane
- Lighter than air
- Trapped by water
- Not a greenhouse gas

Ammonia synthesis

Ammonia production

https://chemengineering.wikispaces.com/Ammonia+production

Current ammonia production plant:
- H_2 via steam methane reforming
- N_2 via cryogenic air separation
- produces 2,000 to 3,000 tons per day
- equivalent 600 – 1,000 MW

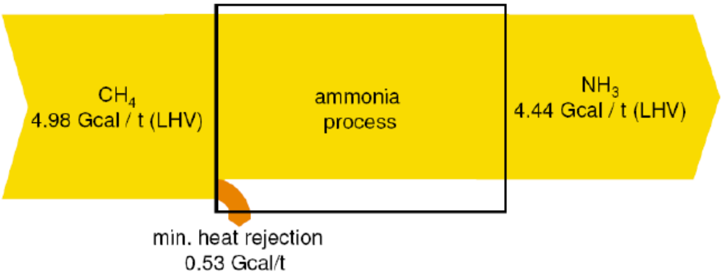


http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/

Disconnect between ammonia production scale and scale of renewables generation

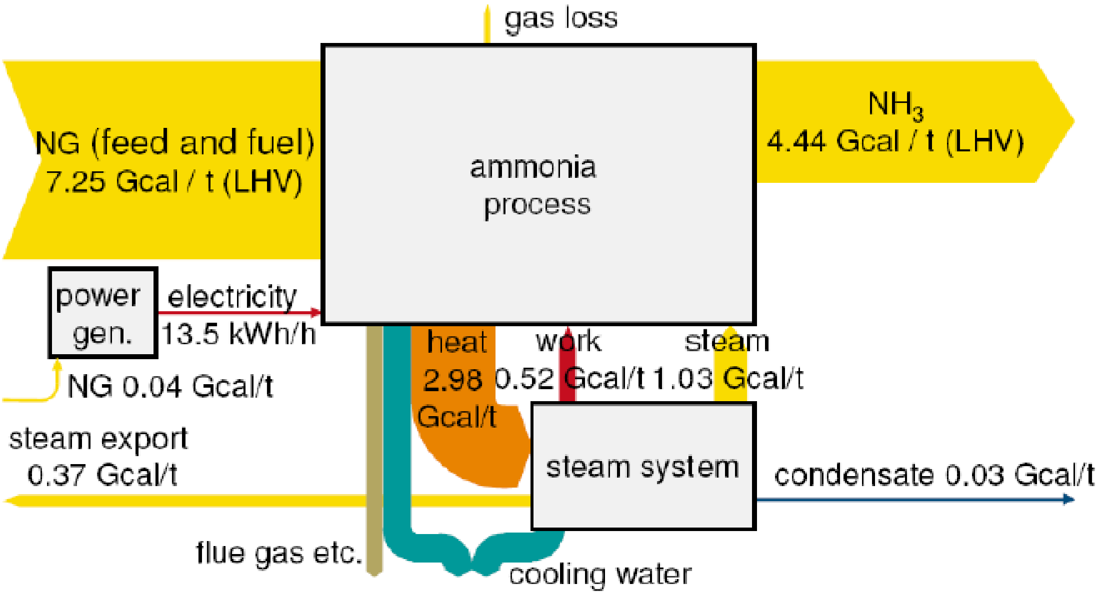
Ammonia production: energy efficiency

Theory



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

Practice

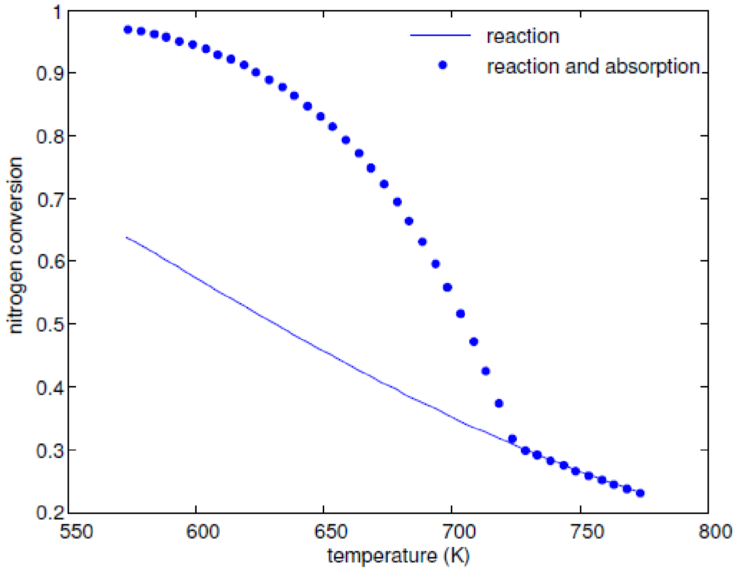


Improving ammonia production

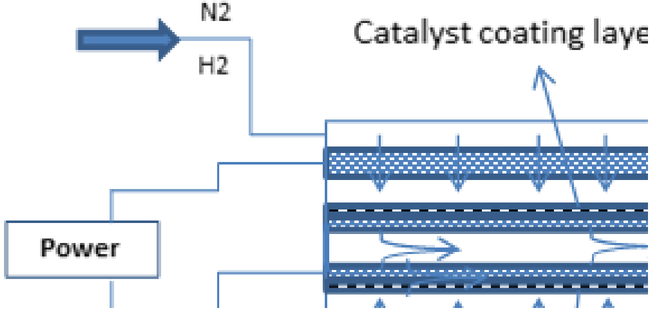
Low pressure ammonia synthesis

Adsorptive enhancement:
Eaton Corp., 2006, Quantumsphere, Inc., 2010, University of Minnesota, 2013
Plasma enhancement:
Global Energies LLC, 2011

Calculated N_2 conversion in the presence of $MgCl_2$ adsorbent



New reactor design

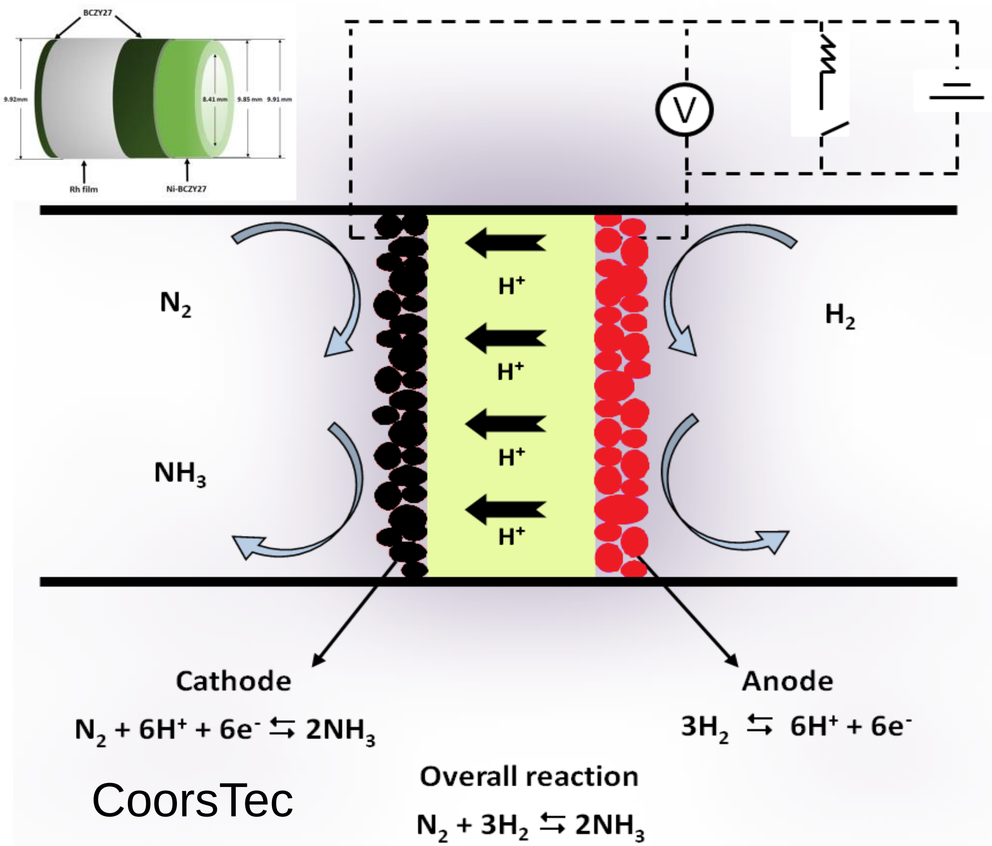


E. Cussler et al. University of Minnesota – Twin Cities

Improving ammonia production

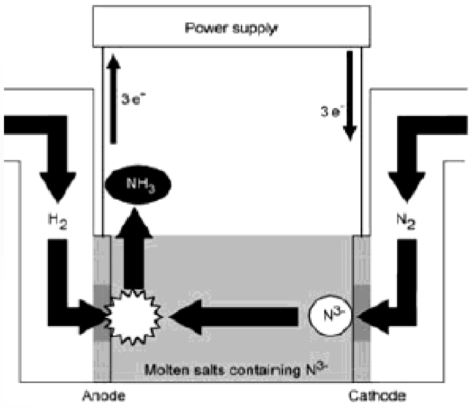
Electrochemical ammonia synthesis

Proton exchange membrane electrolyte

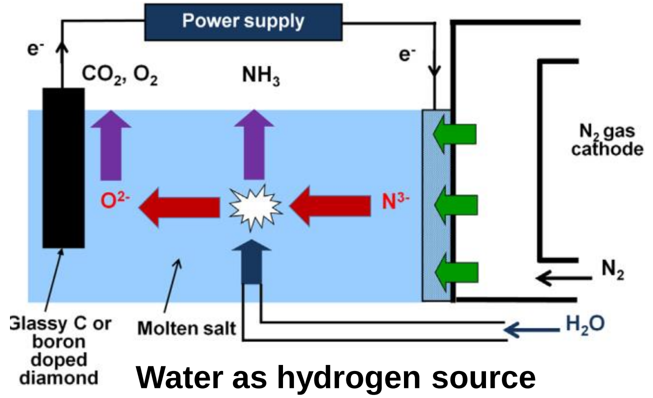


G. Marnellos, M. Stoukides, *Science*, ***282*** (1998) 95.

Molten salt electrolyte



Current efficiency: 72%
Potential: 0.48 V (vs. Li+/Li)
Li+/Li: -3.04 V vs. SHE



T. Murakami et al, *JACS*, **125** (2003)
T. Murakami et al, *Electrochim. Acta*, **50** (2005)
N. Serizawa et al.,*J. Electrochem. Soc.* 159 (2012)

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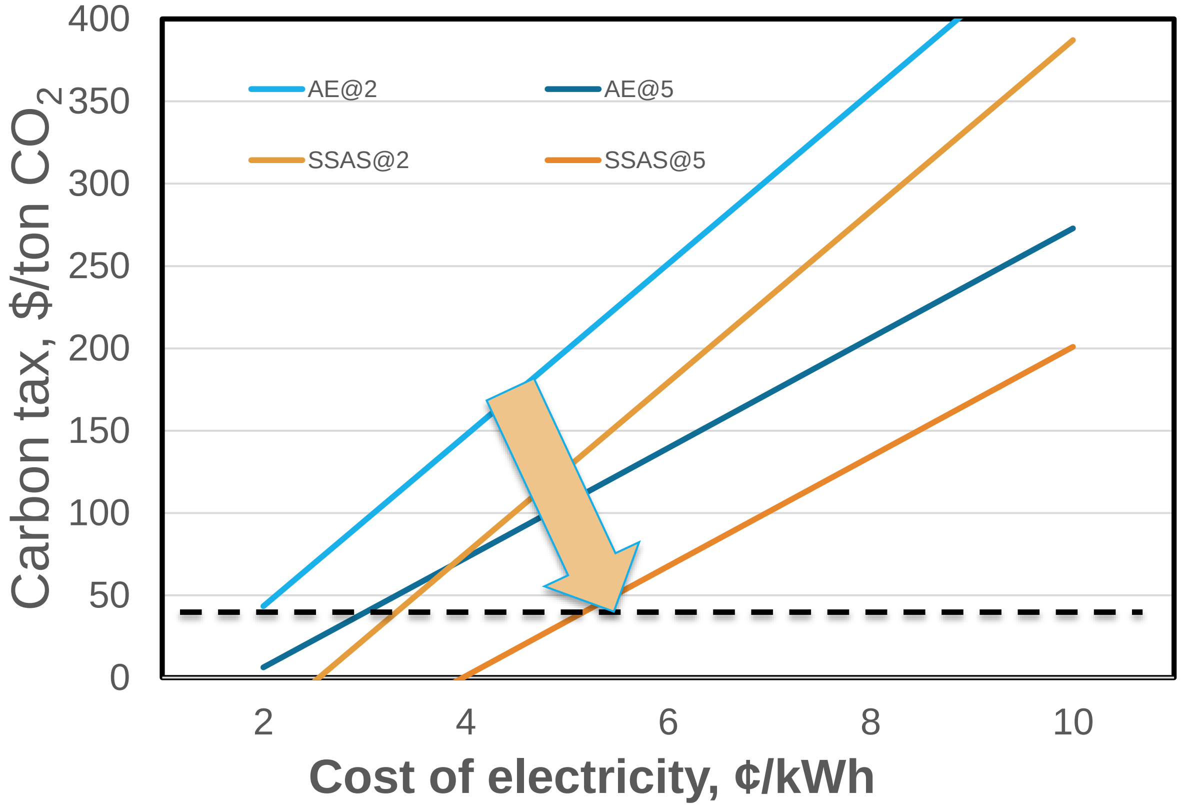
SMR vs. electrolytic hydrogen

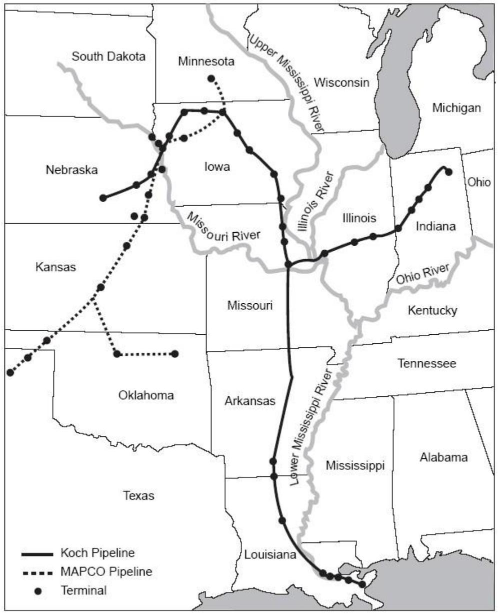
Break even energy cost of ammonia synthesis



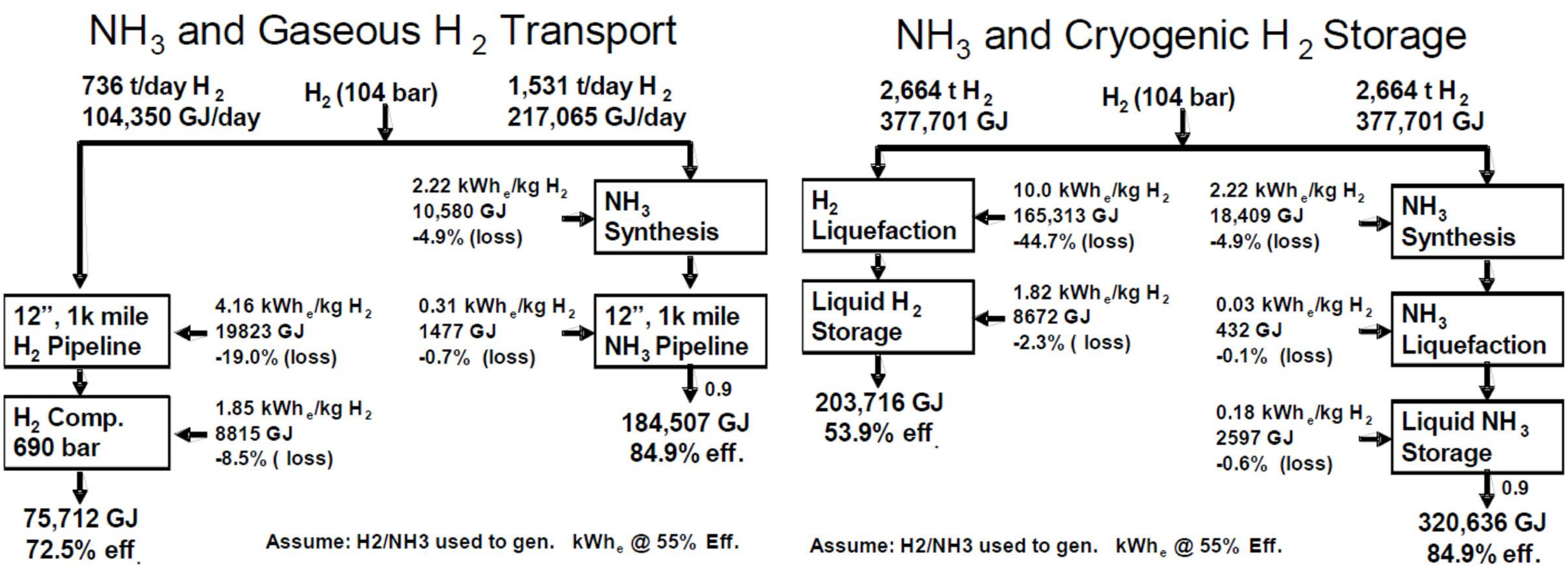
AE- advanced electrolysis, SSAS – solid state ammonia synthesis, NG prices from 2 to 5 $/MBtu

Hydrogen Cost ($/kg) = 0.286*NG price ($/MMBtu) + 0.15 Penner

Ammonia for energy transportation



Comparison of NH_3 and H_2 transportation and storage



N Olson and J. Holbrook, 2007

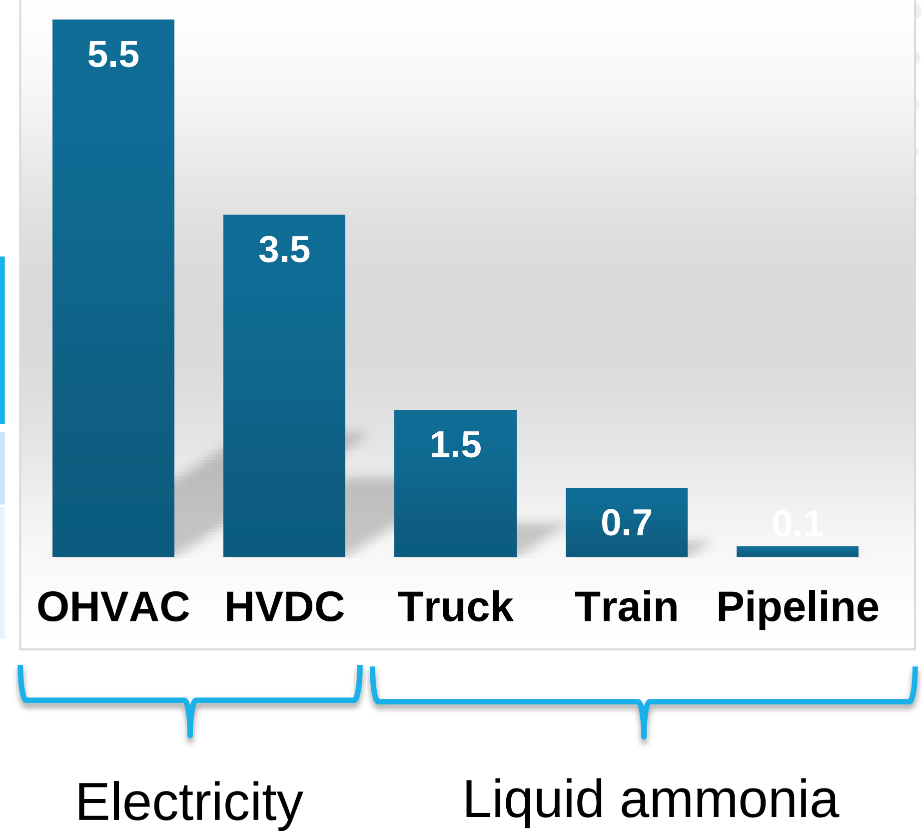
Energy transportation capacity and losses

Energy transmission capacity
(at the same capital cost)

	Power line	CH_2 (350 bar)	Liquid NH_3
Capacity	1.2 GW	6.5GW	41GW
Protective zone	50-70 m	10 m	10 m

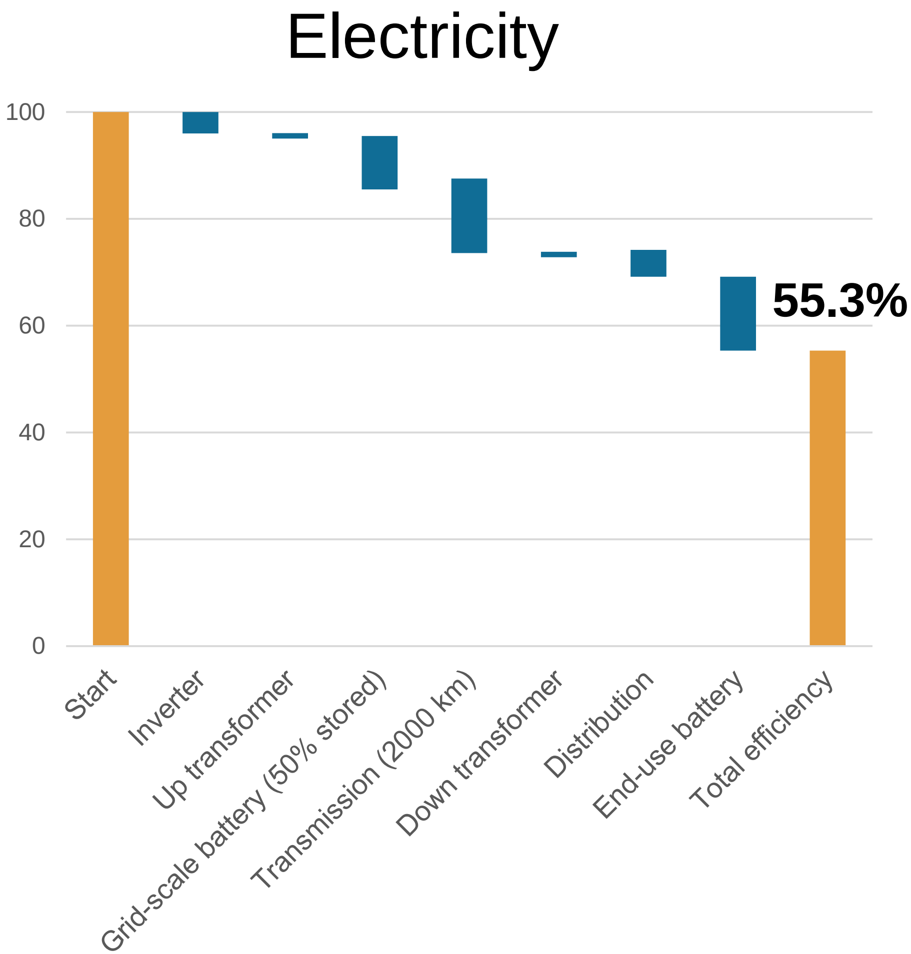
D. Stolten (Institute of Electrochemical Process Engineering), BASF Science Symposium, 2015

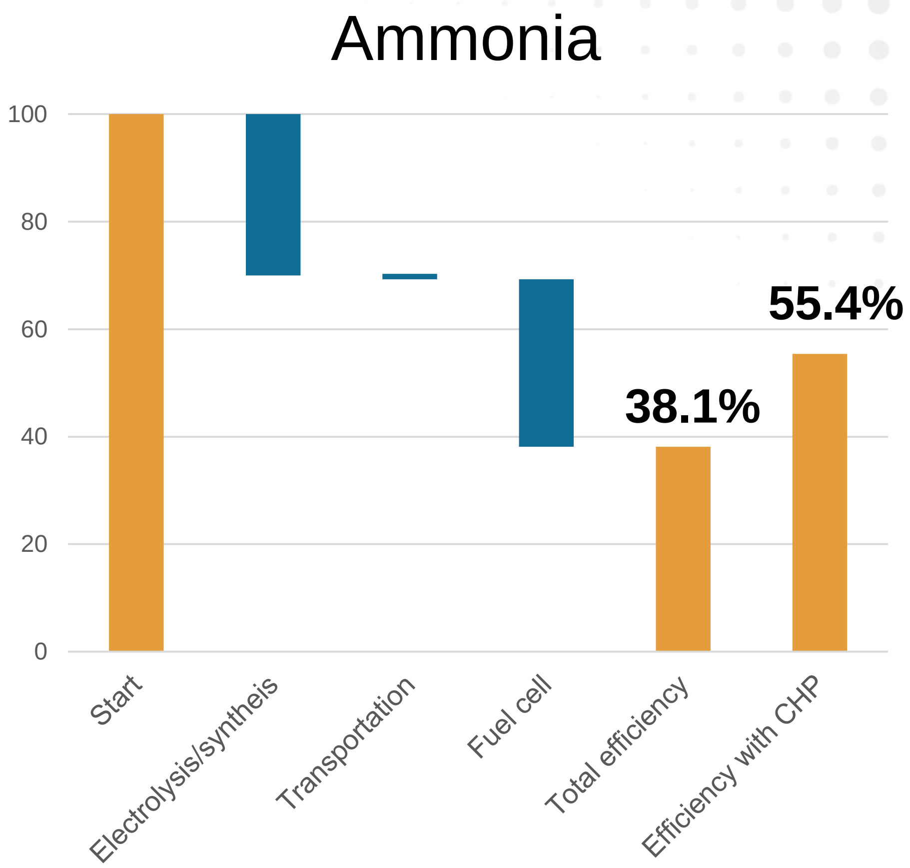
Energy transmission losses (% per 1000 km)



Liquid pipelines have highest capacity and efficiency

Energy transportation efficiency (2000 km)





Electricity transportation is more efficient…if we can use it directly

Ammonia as energy storage media

Energy storage comparison

30,000 gallon underground tank contains 200 MWh (plus 600 MMBTU CHP heat

Capital cost ~$100K

=

204 MWh NGK battery in Japan

or

40 x 

5 MWh A123 battery in Chile

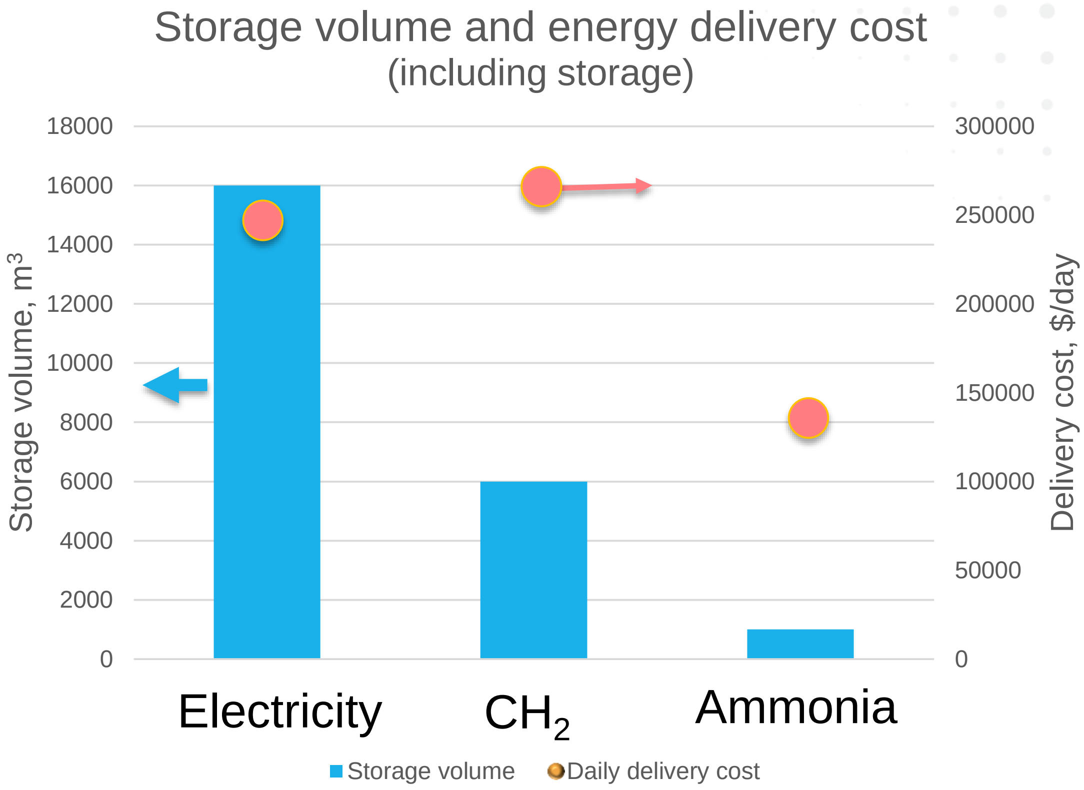
Capital cost $50,000 - 100,000K

Ammonia provides smallest footprint and CAPEX

Cost of energy storage and transportation

Case study
Solar PV array 500 MW
8 hrs active, storage capacity 50%
4 GWh electricity or 120,000 kg H_2
or 860 ton NH_3
Delivery from Utah to East Coast
(2000 miles)
Power line capital cost $16.2M/mile

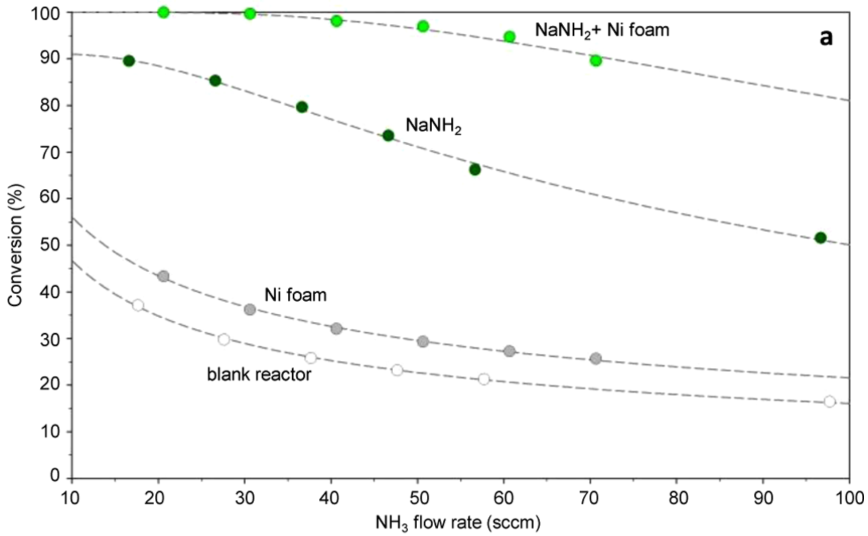
DuraTrack™ PV array



Ammonia as hydrogen carrier

Ammonia cracking

Breakthrough in catalyst design



W. David et al., *J. Am. Chem. Soc.*, **136** (2014) 13082
J. Guo et al., *ACS Catal*., **5** (2015) 2708

Ammonia electrolysis

(Ohio University)

Low cell potential (E^0 = 0.077V)
Theoretical efficiency 95%

B. Boggs et al., *J. Power Sources* **192** (2009) 573

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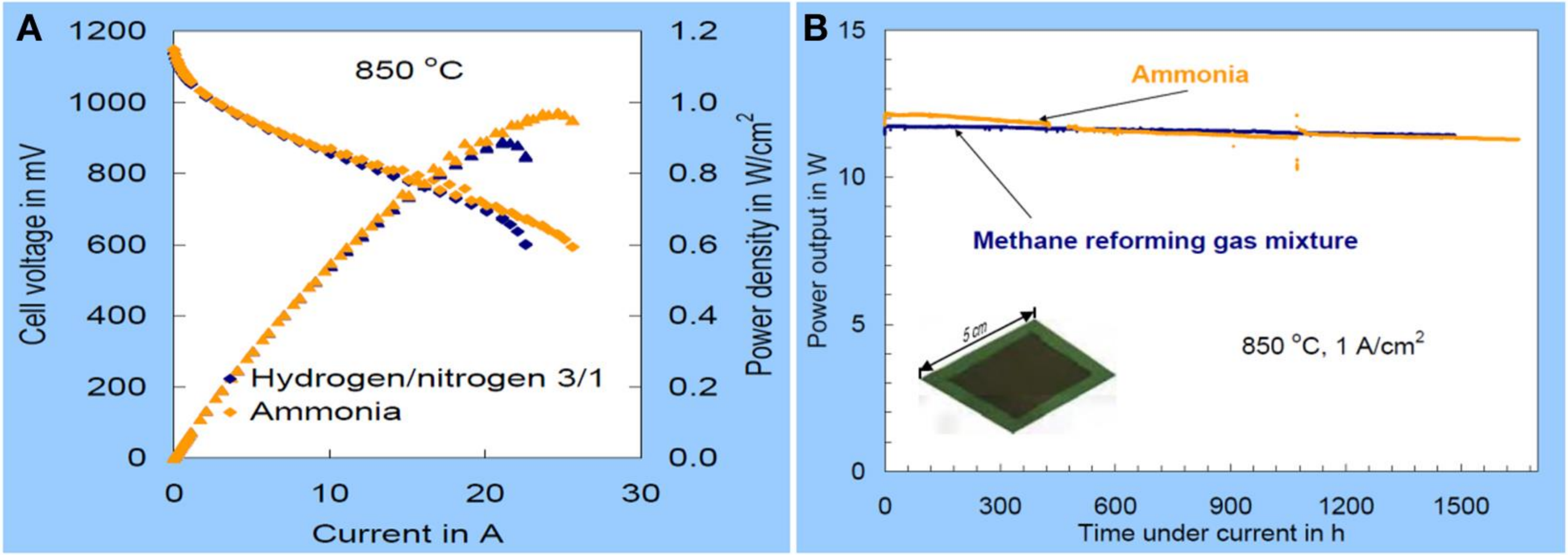
Ammonia as a fuel for fuel cells

- Alkaline fuel cells
- Molten carbonate fuel cells
- Protonic conductor fuel cells
- Solid oxide fuel cells



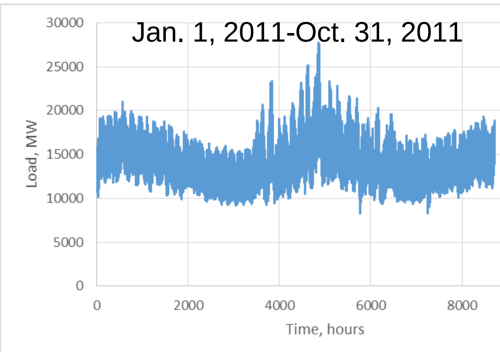
A. Hagen, Use of alternative fuels in solid oxide fuel cells, 2007

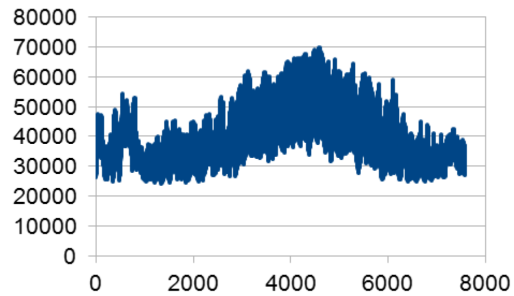
Use ammonia for long-time energy storage

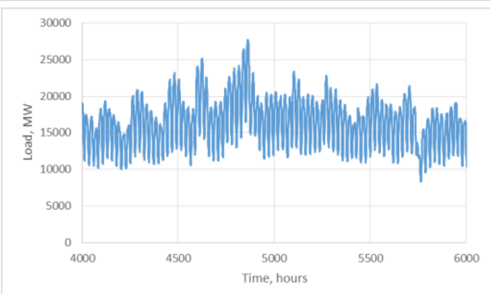
Daily electric load curve

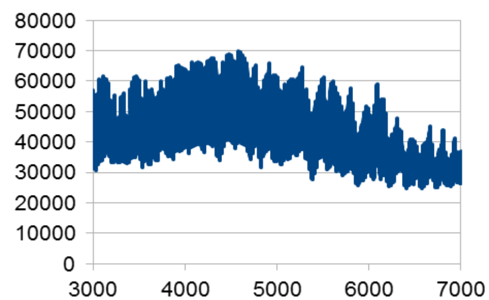
ISO-New England

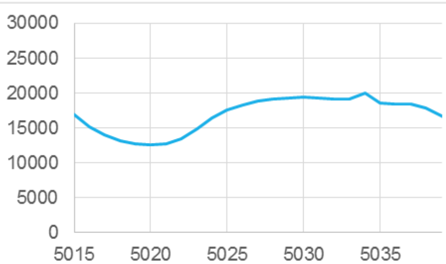
ERCOT (Texas)

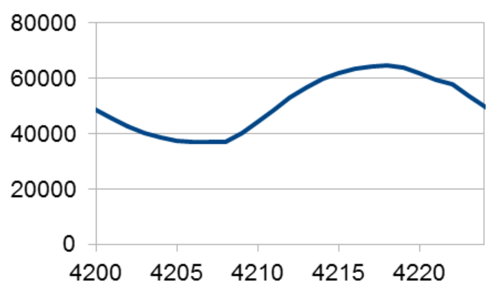






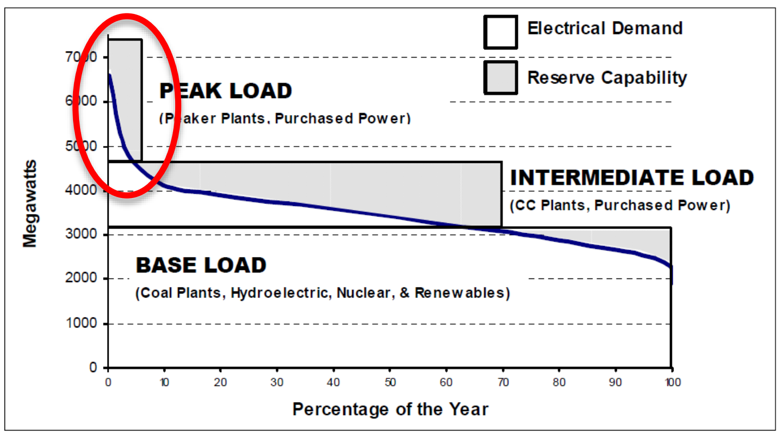






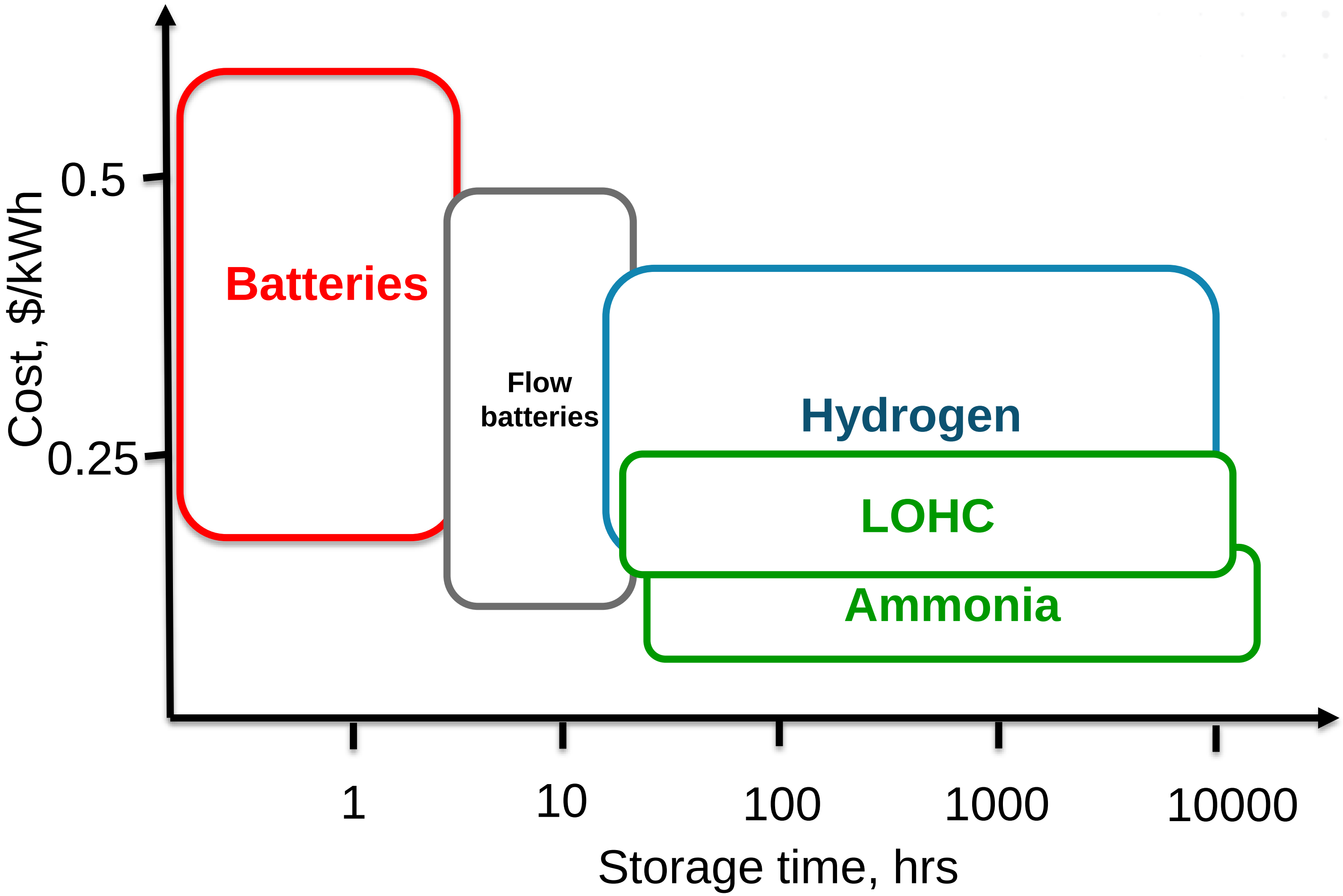
- Maximum load variation ~15GW
- Average seasonal variation ~5GW
- Different seasonal pattern but similar daily profile

Opportunities for energy storage in liquids



Public Service Commission of Wisconsin Report, 2011

Levelized cost of energy storage



New ARPA-E Program: Renewable Energy to Fuels through Utilization of Energy-dense Liquids (REFUEL)

Program Director:
Grigorii Soloveichik

Planned program launch 2016

Please note:

- The REFUEL FOA was issued on April 26, 2016 and is in the quiet period
- In the event of any inconsistency between this presentation and the REFUEL FOA, the latter will control.
- Amendments to the FOA, if any, are published on eXCHANGE.

How to increase penetration of renewable energy?

Critical needs

- Remote renewable power generation separated from local energy consumption (electricity + transportation fuels)
- Wide spread of intermittent renewables requires bulk energy storage
- Infrastructure for renewable power transmission and distribution needs to be build and will be expensive

Proposed solution

Combine energy transportation and storage and use the existing infrastructure via:

i) conversion of renewable power, water and air into hydrogen-rich carbon neutral liquid fuels,
ii) transportation of liquids, and
iii) energy generation at the end point using direct (electrochemical) or indirect (via intermediate hydrogen extraction) fuel cells

Renewable energy storage and delivery via liquid fuels – application space

Synthesis of liquid fuels | Fuels transportation | **Application space**

Category 1

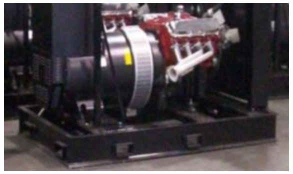
Air

Water

Category 2

Direct use (blending) in ICE vehicles (drop-in fuel)

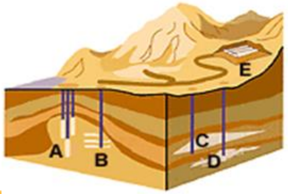
Direct use in stationary gensets



Medium to long term energy storage

Hydrogen generation for fueling stations

Seasonal energy storage



- Energy delivery from remote locations
- Energy delivery from stranded sources
- Energy storage and delivery combined

Renewable Energy to Fuels through Utilization of Energy-dense Liquids (REFUEL)

Program goals

- Develop small to medium scale direct conversion of renewable energy to high energy density liquid fuels
- Develop cost effective methods for fuels conversion to electricity or H_2

Project targets

- Competitive cost of delivered energy
- Demonstration of fuel synthesis and conversion in a bench scale prototype

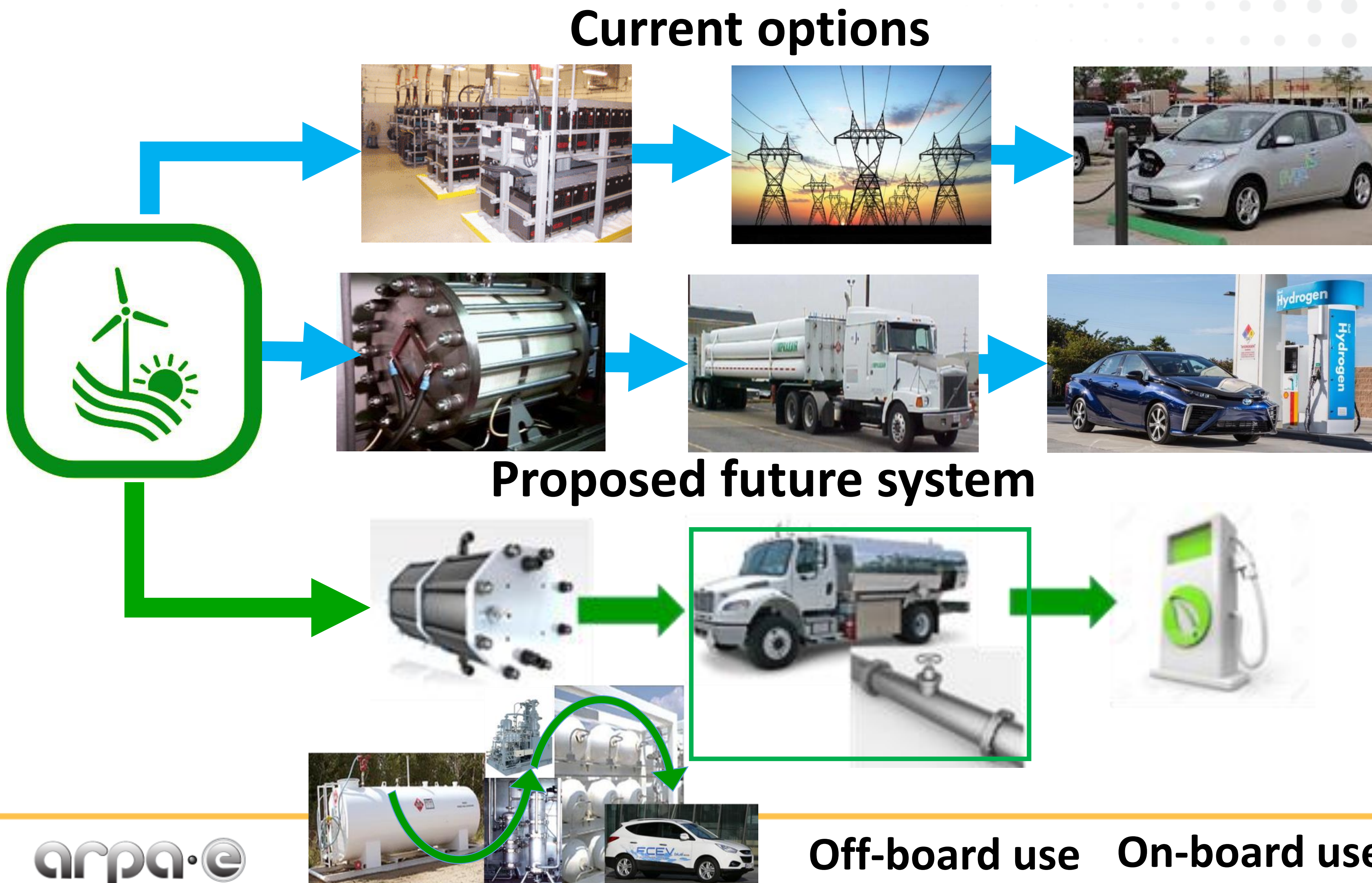
Potential program benefits

- Reduced transportation losses
- Providing long-term energy storage with low cost/footprint
- Use of existing liquid fuel infrastructure
- Enabling fuel cell car fueling stations
- Reduced CO_2 emissions and oil imports

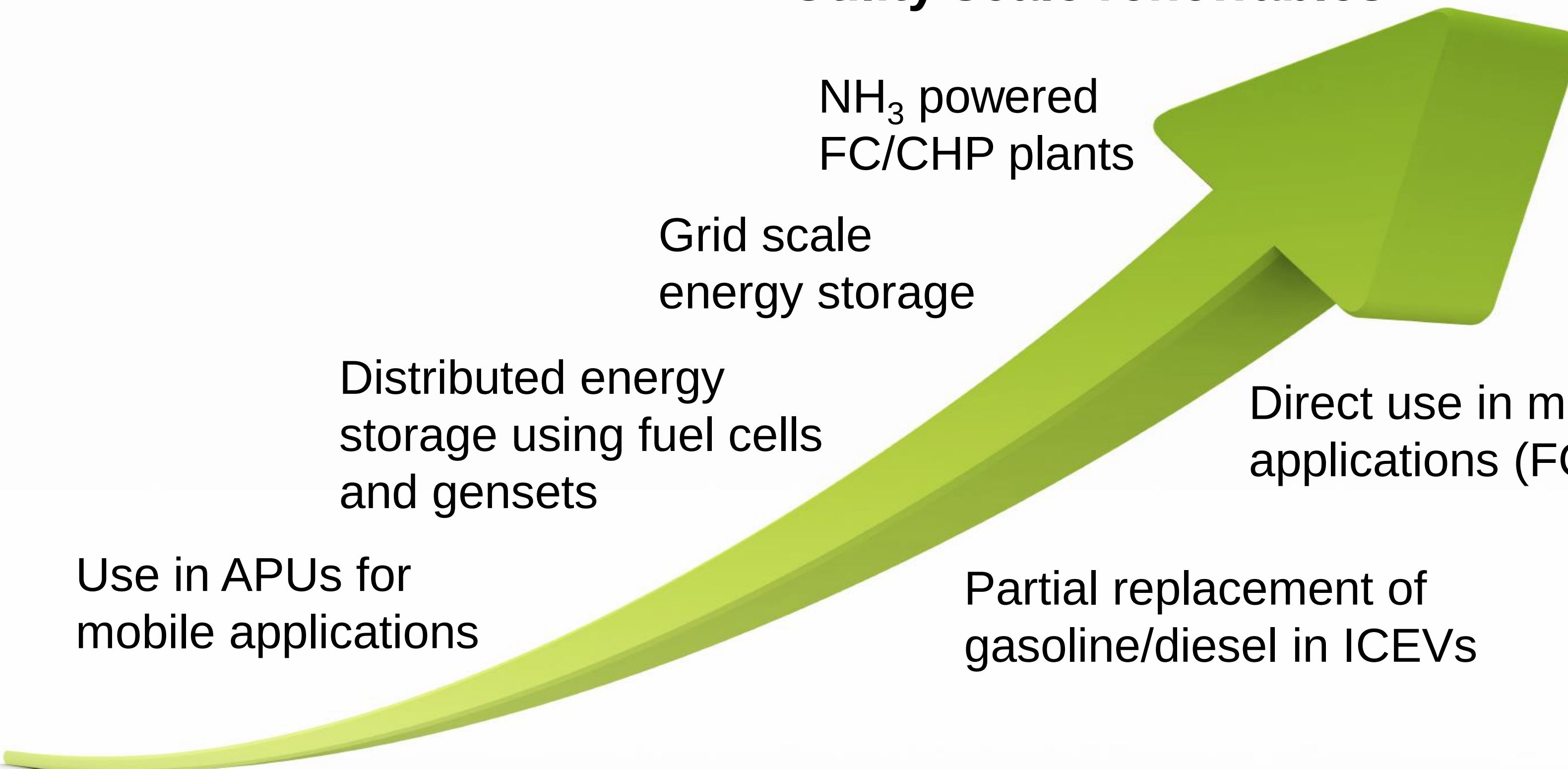
Potential benefits of ammonia based energy storage and delivery system

- Reduced transportation losses
- Smaller storage footprint
- Use of existing liquid fuel infrastructure technologies
- Long-term energy storage
- Enabling fuel cell car fueling stations
- Increased safety
- Reduced CO_2 emissions
- Reduced imports

Energy delivery from remote renewable production



Potential markets



Transformational change in bringing more renewable energy to market

Ammonia related projects funded by ARPA-E

OPEN 2015

Electrochemical Ammonia Synthesis for Grid Scale Energy Storage

Shekar Balagopal, Ceramatec, Inc. *(partners with UNM and LANL)*

A lower temperature and higher efficiency membrane process to electro-synthesize ammonia at 150 -300 C utilizing a solid electrolyte membrane reactor will be developed. Two types of ion conducting solid membranes; a lithium ion conductor and a proton conductor, will be investigated.

NH_3 Synthesis for Energy Storage, Fuel, and Agriculture Applications

Joseph Beach, Starfire Energy *(partners with Colorado School of Mines)*

A low temperature and pressure technology for distributed generation of ammonia using enhanced catalysis and novel reactor design will be developed.

IDEAS

Low Cost Membrane Reactor Synthesis of Ammonia at Moderate Conditions

J. Douglas Way, Colorado School of Mines

A new membrane reactor configuration to achieve NH_3 synthesis at moderate pressures (below 10 atm) and temperatures (≤ 600 °C) will be developed based on low cost hydrogen permeable membranes.

Conclusions

- **Ammonia is an ideal candidate for long term energy storage and long distance energy delivery from renewable intermittent sources**
  - high energy density
  - feedstock widely available
  - production successfully scaled up (150MT annually)
  - zero-carbon fuel
  - infrastructure for storage and delivery technologies in place
  - can be used in fuel cells and thermal engines
- **Remaining challenges**
  - down scale of production economically (match renewables)
  - production tolerant to intermittent energy sources
  - improve conversion efficiency to electricity, power or hydrogen
  - improve safety
  - public acceptance/education

20th Century – 1st Ammonia Revolution
- Munitions and fertilizers
21st Century – 2nd Ammonia Revolution?
- Green energy carrier

Why Work at ARPA-E?

- **CONTRIBUTE TO A BETTER ENERGY FUTURE**
  - Work towards creating a more efficient, more secure energy future
- **JOIN OUR INNOVATIVE STARTUP-LIKE CULTURE**
  - ARPA-E is a fast-paced, collaborative Agency
- **WORK IN DIVERSE TECH AREAS**
  - At ARPA-E you'll have the opportunity to work with a diversity of energy issues and explore new fields
- **COLLABORATE WITH OTHER EXPERTS**
  - Work with other experts from many different disciplines who are devoted to creating a better energy future

If you are interested in applying or learning more, please email arpa-e-jobs@hq.doe.gov

ARPA-E Recruitment Opportunities

Want to work at ARPA-E? There may be a role for you!

Program Director

- Program development
- Active project management
- Thought leadership
- Explore new technical areas

Technology-to-Market Advisor

- Business development
- Technical marketing
- Techno-economic analyses
- Stakeholder outreach

Fellow

- Independent energy technology development
- Program Director support
- Organizational support

If you are interested in applying or learning more, please email arpa-e-jobs@hq.doe.gov

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ARPA-E Recruitment Opportunities

ARPA-E is currently hiring new Program Directors
What makes an ideal candidate?

Roles, Responsibilities, and Attributes

Program Development

- Perform technical deep dive to solicit input from multiple stakeholders in the R&D community
- Present & defend program concept in climate of constructive criticism

Active Project Management

- Actively manage portfolio projects from merit reviews through project completion
- Extensive "hands-on" work with awardees

Thought leadership

- Represents ARPA-E as a thought leader in the program area

- R&D experience; intellectual integrity & flexibility; technical breadth; commitment to energy; communication skills; leadership; and team management
- *Confidence, but not arrogance*

If you are interested in applying or learning more, please contact a current ARPA-E Program Director or email arpa-e-jobs@hq.doe.gov

ARPA-E Recruitment Opportunities

ARPA-E is currently hiring new Technology-to-Market Advisors
What makes an ideal candidate?

Roles, Responsibilities, and Attributes

Business Development and Technical Marketing

- Advise project teams on market, strategy, business planning, IP, product development, and supply chain considerations
- Target public and private follow-on funding sources

Techno-Economic Analyses

- Perform techno-economic analyses to inform new programs and funded projects

Stakeholder Outreach

- Represents ARPA-E to a range of stakeholders and represents the Agency as a thought leader in the program area

- 5-25 years of work experience, including technology, research, and business experience; Advanced degree; Strong technical background; Superior analytic skills; strong written and oral communication skills; Demonstrated interest/expertise in energy and energy technologies

If you are interested in applying or learning more, please contact a current ARPA-E Technology-to-Market Advisor or email arpa-e-jobs@hq.doe.gov

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