High-efficiency Nitrogen Oxidation (HNO3)

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HNO3 Proposers Day

December 12, 2025

Agenda

Start	End	Duration	Item
12:30 PM	1:00 PM	0:30	**Check-In/Arrival**
1:00 PM	1:10 PM	0:10	**Welcome and Logistics**
1:10 PM	1:40 PM	0:30	**HNO3 Technical Program Overview** *Dr. Keith Whitener*
1:40 PM	1:55 PM	0:15	**Working with DARPA** *DARPA/Contracts Management Office*
1:55 PM	2:15 PM	0:20	*Break*
All questions submitted to HNO3@darpa.mil by 1:55 PM			
2:15 PM	4:00 PM	1:45	**Lightning Talks** *Teaming presentations (5 min. each)*
4:00 PM	4:15 PM	0:15	*Break*
4:15 PM	5:00 PM	0:45	**Q & A** *Only questions submitted by 1:55 PM will be answered*
5:00 PM Meeting Adjourns			

Proposers submit questions prior to 1:55 PM for Q&A at 4:15 PM
(All attendees: please email HNO3@darpa.mil to submit questions today)

Security & Administrative Items

This Meeting is Being Recorded for Data Archive Purposes

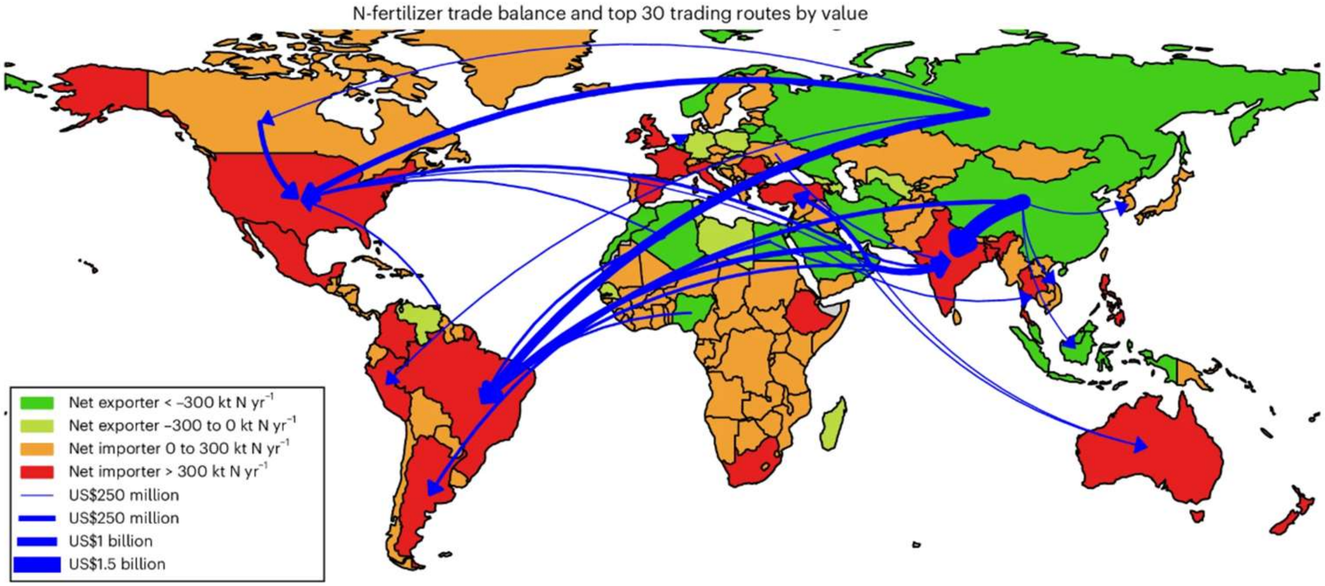
- Meeting Classification Level
  - Unclassified Information
- The meetings participants list is being closely monitored
  - Only registered meeting participants are approved
  - We will admit, mute, and remove participants as needed throughout the event
- Mute yourself when not speaking
  - Moderators will mute participants as needed
  - Call in numbers *6 to unmute (if necessary)
- Screen captures of the data presented is not permitted
  - Please reach out to the DARPA team if you have questions on the information being presented

Administrative Items (cont.)

- The Proposers Day briefing is intended to provide an orientation to the HNO3 Broad Agency Announcement (BAA) and is solely for information purposes
- The solicitation supersedes anything presented or said by DARPA at the Proposers Day: In the event of a BAA posting, if there is any discrepancy between what is presented today and the anticipated BAA, the BAA takes precedence.
- Examples in this briefing (e.g., technologies, use cases) are chosen for ease of illustration only and do not constitute endorsement of any particular approach
- Interested performers are expected to be able to articulate a clear and compelling vision for their technology, proposed course of research, and transition potential
- We need your help to make this program a success!

HNO3 Program Vision

Problem: Nitric acid, a crucial ingredient for explosives and propellants, requires significant energy and large infrastructure, and the U.S. depends heavily on foreign sources for upstream supply



Mignolla and Rosa, *Nature Food* **2025**, *6*, 610-621

HNO3 will contribute to:

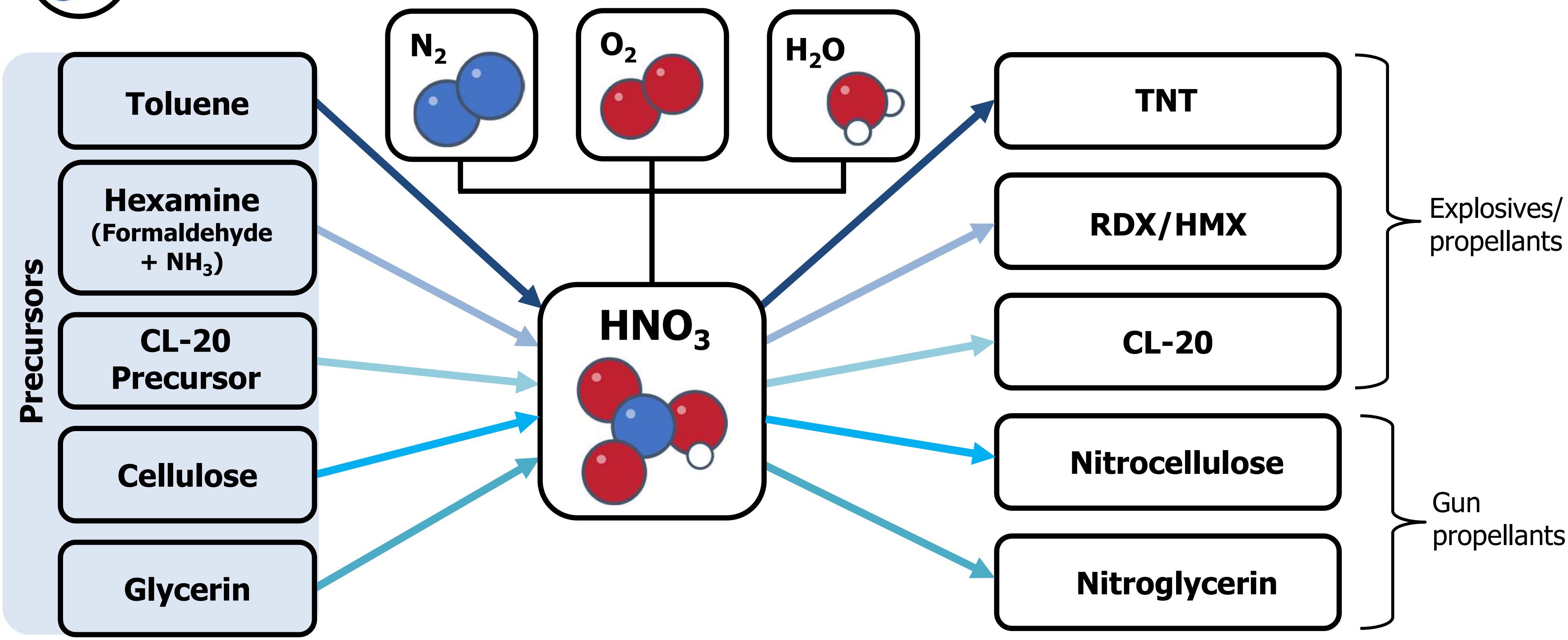
1. Securing a key defense- and civilian-relevant chemical against supply chain shocks
2. Decentralizing production to mitigate the danger of transporting and storing large quantities of reactive materials
3. Lowering the resources required to produce 60+ million tons/year of HNO_3

H1: HNO3 will demonstrate efficient, scalable nitric acid manufacturing from air and water

HNO_3: Nitric acid

Centrality of HNO3 in Defense-relevant Chemistry

Defense Energetics: Nitric acid is a critical precursor for all energetics



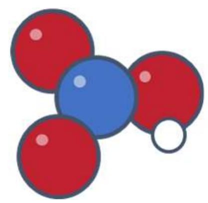
CL-20: Hexanitrohexaazaisowurtzitane
H_2: Molecular hydrogen
H_2O: Water

HMX: Octogen
HNO_3: Nitric acid

O_2: Molecular oxygen
RDX: Hexogen
TNT: Trinitrotoluene

Nitric Acid: Critical Chemical for Defense and Industry

HNO_3



Defense Energetics

- Manufacture <u>all</u> explosives in U.S. arsenal
- Oxidizers for propellants

Chemical Manufacturing

- Adipic acid → Nylon
- TDI → Polyurethane foams
- Nitrobenzene → aniline → dyes & rubber
- Nitrocellulose → coatings & adhesives

Mining & Construction

- Earth moving for large scale civil infrastructure
- Open pit rock breaking
- Precision demolitions

Pharmaceuticals

- Nitroglycerin → heart medications
- Nitrofurantoin → antibiotics
- Silver nitrate → wound care

Fertilizers & Agriculture

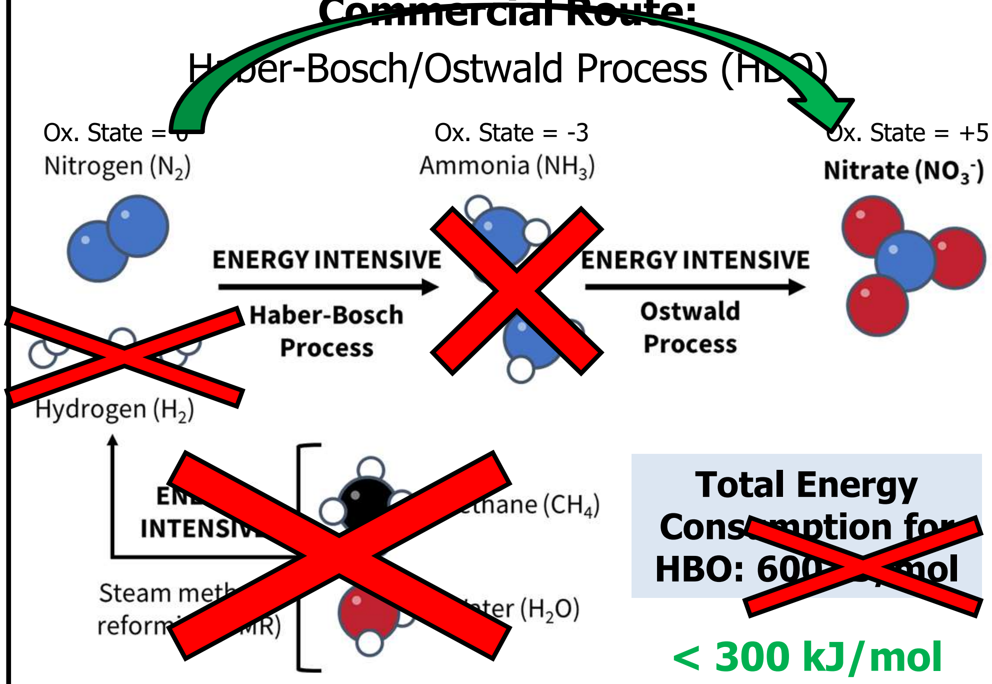
- Nitrate-based fertilizers
- Supports the global supply chain → 40-60% of the global crop yields

TDI: Toluene diisocyanate
HNO_3: Nitric acid

How It's Done Today: Efficiency/Centralization Tradeoff

Commercial Route:

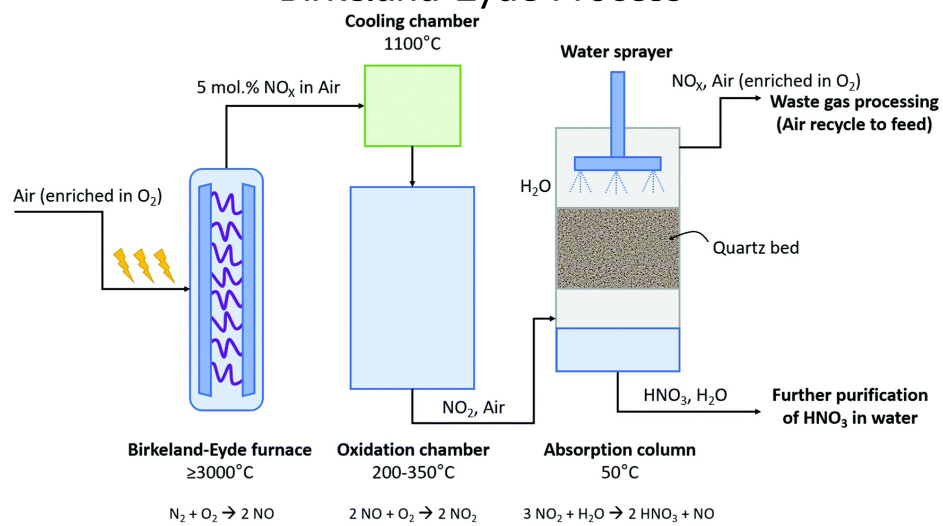
Haber-Bosch/Ostwald Process (HBO)



HBO is inefficient and difficult to decentralize

Decentralized Plasma Route:

Birkeland-Eyde Process



- Amenable to decentralized production
- 5x more energy than HBO

No clear path towards improving efficiency

Electrochemical nitrogen oxidation can enable a more energy-efficient and decentralized route to nitric acid production

Ox. State: Oxidation state

Nitrogen Oxidation: Fundamentals

Activation of N_2

$N \equiv N$

Bond Strength = 941 kJ/mol

One of the strongest bonds in nature!

Oxidation of N_2

$$N_2 + \frac{5}{2}O_2 + H_2O \rightarrow 2HNO_3$$

$$\Delta H^o_{rxn} = -13.5\ kJ/mol$$

This reaction is exothermic!*

Nitrogen oxidation is a catalysis + mass transport problem

Electrochemistry: Coupling nitrogen/water reaction with oxygen reduction gives us nitrate almost for free

Nitrogen Oxidation Reaction (NOR) $N_2 + 6H_2O \rightarrow 2NO_3^- + 12H^+ + 10e^-$ $E^\circ = -1.31\ V\ vs.\ RHE$

Oxygen Reduction Reaction (ORR) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^\circ = +1.23\ V\ vs.\ RHE$

RHE: Reversible hydrogen electrode
E°: Standard electrode potential
ΔH^o_{rxn}: Standard enthalpy of reaction
ΔG^o_{rxn}: Standard Gibbs Free Energy of reaction

*$\Delta G^o_{rxn} = +87\ kJ/mol$

Challenges and Solutions for Direct Nitrogen Oxidation to HNO_3

Challenges

Competition with the OER

NOR: $N_2 + 6H_2O \rightarrow 2NO_3^- + 12H^+ + 10e^-$ $E^\circ = -1.31\ V\ vs.\ RHE$

OER: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E^\circ = -1.23\ V\ vs.\ RHE$

Low solubility of N_2

- 20 mg/L at 298 K, 1 atm *in pure water*
- Increasing ionic strength decreases solubility
- Simple solutions like increasing pressure are limited by reactor design

Slow diffusion of N_2

Results in Poor Mass Transport of N_2
→ Limiting the Rate of NOR

Result: Low rate (0.1-1 nmol s^{-1} cm^{-2}), high energy (> 500 kJ/mol more than necessary)

Solutions

Catalyst design and control

- Static Catalysis: Develop a catalyst that selectively promotes NOR over OER
- Dynamic Catalysis: Dynamic control to increase the rate of NOR

Critical to integrate both approaches to achieve metrics

Reactor design and mass transport control

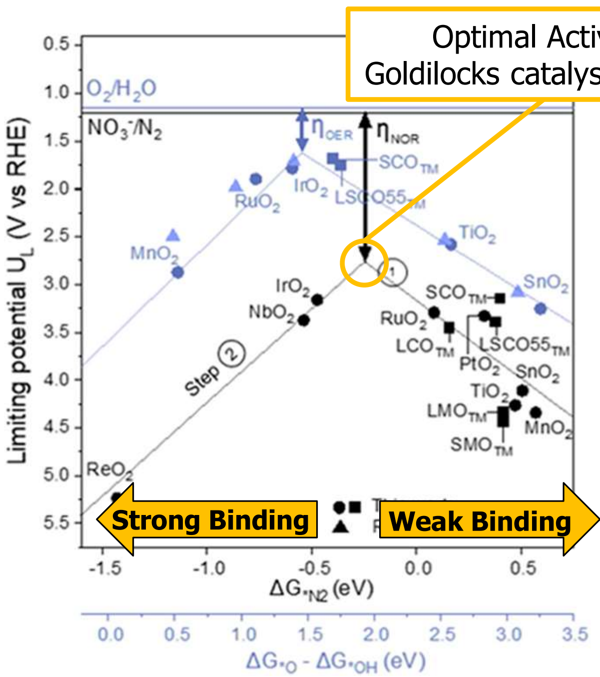
- Increase N_2 solubility and diffusion to active catalytic sites
- Exclude or eliminate water from catalytic sites

Increase rate, decrease energy and unwanted side products

OER: Oxygen evolution reaction
NOR: Nitrogen oxidation reaction

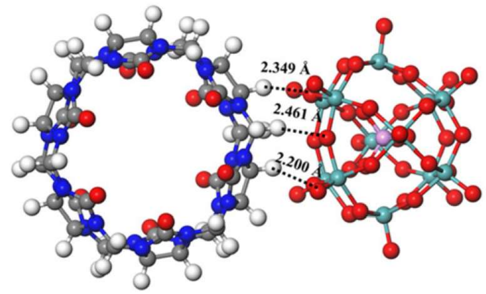
Catalysis Design and Control: Static to Improve Selectivity

Traditional volcano plot analysis



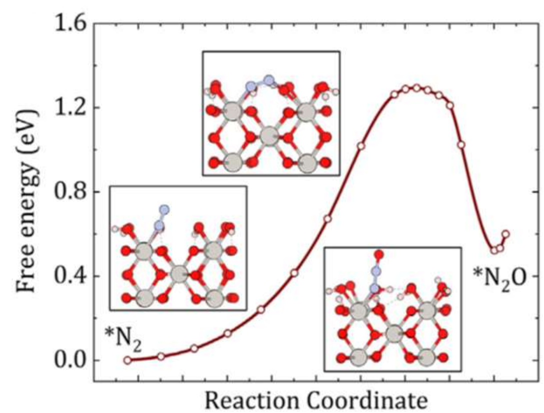
Iriawan et al. *ACS Catalysis* 2025, 15, 8, 6315–6333.

Q[6]-PMA with Mo center



Xu et al. *Inorg. Chem. Front.*, **2024**, *11*, 1117–1122.
Singh et al. *Small*, **2024**, *20*, 2406718.

New catalysts can suppress OER, raise **NOR FE to 50-70%**



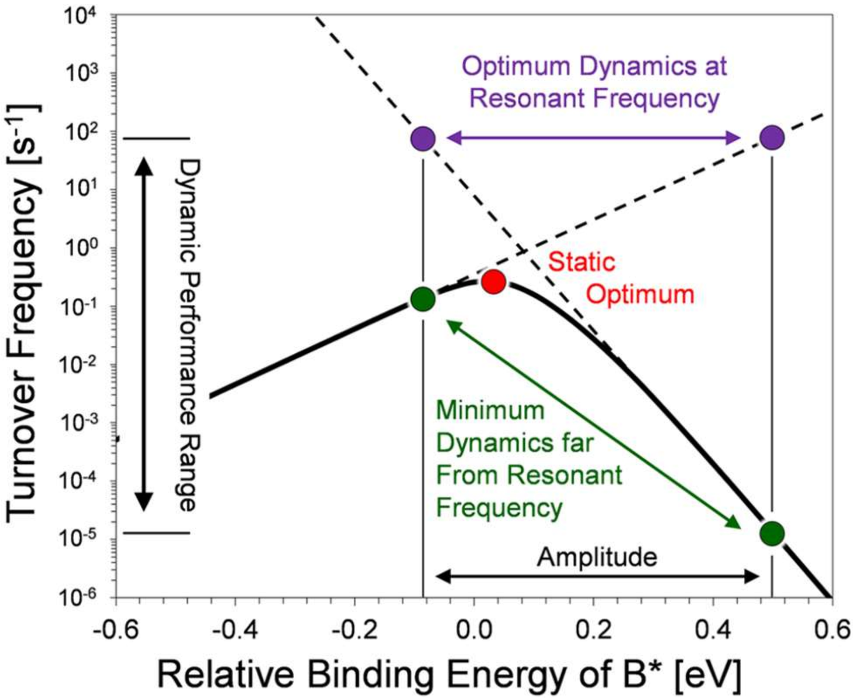
Prajapati et al. *Chem Catal.* **2025**, *5*, 101220.

Modeling provides mechanistic insights for designing catalysts that suppress side reactions, boost desired NOR

Enhancing catalytic performance will require developing catalysts with strong NOR selectivity while minimizing OER activity

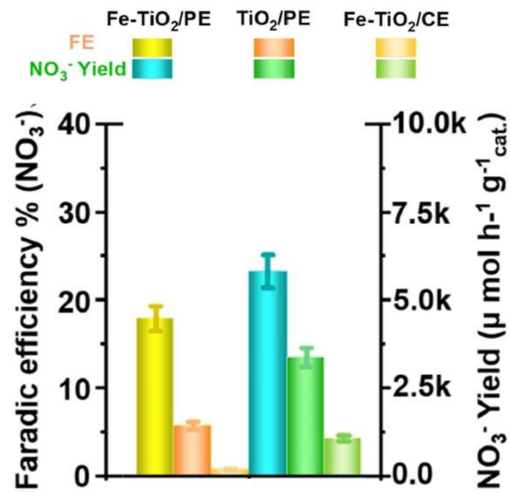
OER: Oxygen evolution reaction
NOR: Nitrogen oxidation reaction
Q[6]-PMA: Cucurbit[6]uril pyromellitic acid
FE: Faradaic efficiency

Catalysis Design and Control: Dynamic to Boost Rate



Ardagh et al. ACS Catal. 2019, 9, 6929−6937

Evidence that voltage swing resonance can **increase NOR rate 45x**, suppress OER



Guo et al., Angew. Chem. Int. Ed. 2023, 62, e202217635

Dynamic catalyst control is key to boosting the rate of NOR

Integrating static and dynamic catalysis is essential to achieving the goals of HNO3

NOR: Nitrogen oxidation reaction
OER: Oxygen evolution reaction

Reactor Design and Mass Transport Control: Solubility & Diffusion

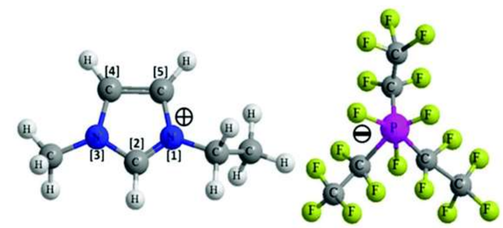
$$i_l = \frac{nFD_{N2}C_b}{\delta}$$

Key Variable	Meaning	Value		
C_b	Bulk concentration	~1 mM	→	**> 50 mM**
δ	Diffusion Boundary Layer	~100 µm	→	**< 300 nm**
i_l	Limiting current density	**0.7 mA/cm²**	→	**> 1 A/cm²**

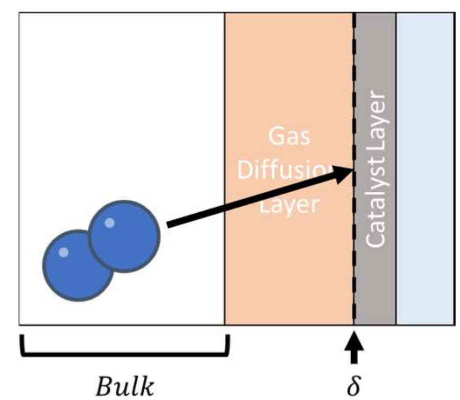
Fluorinated ionic liquids increase N_2 solubility >50x over water

Redesigning reactor as gas diffusion electrode: $\delta \rightarrow 300nm$ or less

Fluorinated ionic liquids



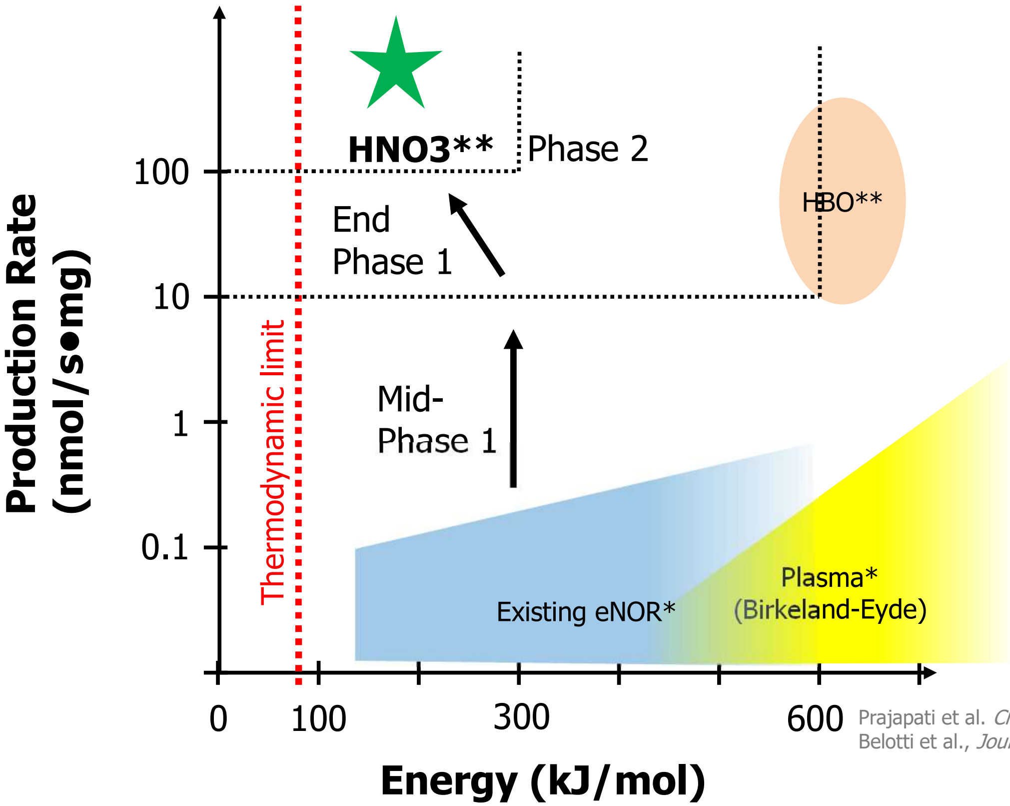
Electrode design



Li et al. *J. Am. Chem. Soc.* 2024, 146, 37, 25569-25577

n: Number of electrons per reaction
F: Faraday's constant
D_{N2}: N_2 diffusion constant

HNO3: Scientific Bottom Line



Prajapati et al. *Chem Catalysis,* **2025**, *5*, 101220
Belotti et al., *Joule,* **2025**, *9*, 101924

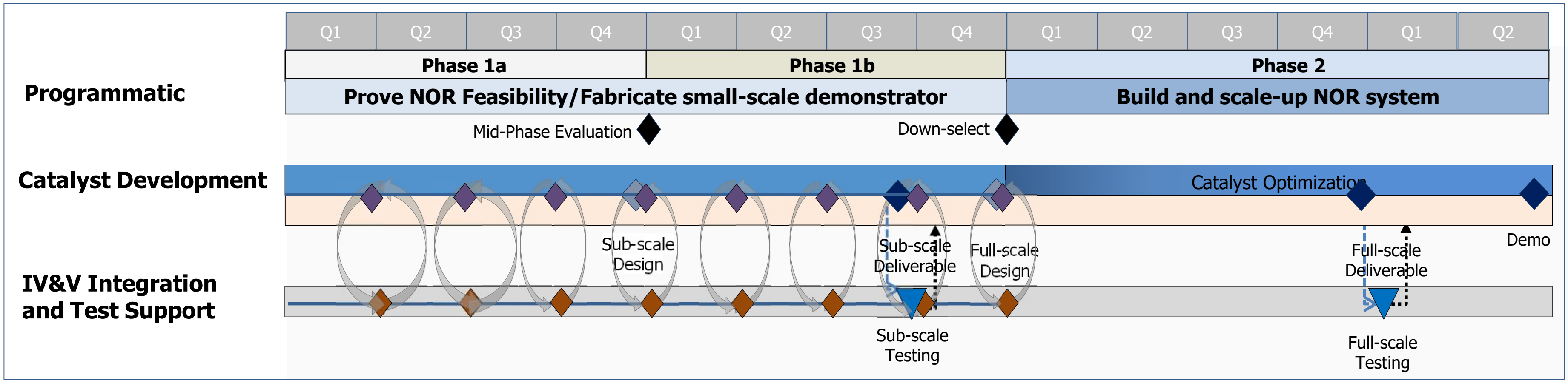
Summary of scientific opportunities

- Current electrochemical NOR rates and energies are **too low to be useful or economical**
- Raising reaction rates simultaneously lowers energy requirements
- Catalysis and mass transport control together can increase rate by **1000-10000x**, bringing down energy requirements to **< 300 kJ/mol**

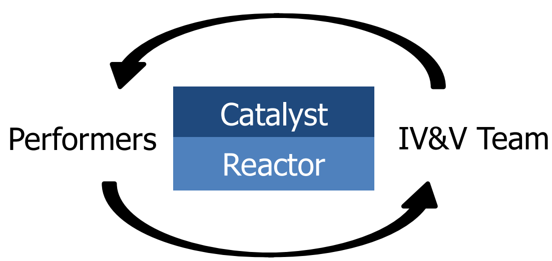
*Includes only the main nitrogen oxidation reaction
**Includes all ancillary energy requirements

HBO: Haber-Bosch-Ostwald process
eNOR: Electrochemical nitrogen oxidation reaction

Program Structure



Catalyst Quarterly Deliverables
Quarterly IV&V Catalyst Evaluation



Performers and IV&V are involved in all aspects of development

IV&V Team Responsibilities:

- Quarterly evaluation of performers' NOR catalysts by rapid integration into existing reactor
- Oversee testing and evaluation of prototypes
- Advise on reactor design throughout all phases

IV&V: Independent verification and validation
NOR: Nitrogen oxidation reaction

Metrics

Metric	Mid-Phase 1 (12 mo)	End Phase 1 (12 mo)	Phase 2 (18 mo)
Reaction Rate	> 10 nmol s^{-1} cm^{-2} Or > 10 nmol s^{-1} mg_{cat}^{-1}	> 100 nmol s^{-1} cm^{-2} Or > 100 nmol s^{-1} mg_{cat}^{-1}	-
Energy	< 600 kJ/mol_{HNO3} (reaction only)*	< 300 kJ/mol_{HNO3} (reaction only)*	-
Minimize side products	-	$Yield_{NOR} > 5 \times Yield_{side\ rxns}$	$Yield_{NOR} > 7 \times Yield_{side\ rxns}$
Production Rate	-	1 L/day lab grade 68% HNO_3 from air and water	50 L/day lab grade 68% HNO_3 from air and water
SWaP	-	< 1 kW**	< 4 kW** < 4 m^2 footprint

*Excludes secondary processing for reagent purification, product concentration, etc.
**Includes all energy costs (such as the ones above) for generating lab grade 68% HNO_3

Cat: Catalyst
HNO_3: Nitric acid
NOR: Nitrogen oxidation reaction
RXNS: Reactions

HNO3 Proposal Outline

Proposals must include:

- A detailed technical rationale of how the proposed method can achieve the program goals and metrics, including supporting empirical data, relevant literature citations, and calculations. Any quantitative performance figures must be supported by discussion or mathematical theory.
- An initial selection of a catalyst material for direct nitrogen oxidation along with a detailed justification for its selection.
- An initial concept design of the reactor for direct nitrogen oxidation and a detailed justification for the design.
- A comprehensive plan for designing a sub-scale reactor, including detailed strategy for scaling up to a full-scale reactor capable of achieving the metrics for nitric acid generation. The plan must include a discussion of the scalability of reactor design, addressing potential challenges and considerations associated with scaling from sub-scale to full-scale.
- An analysis plan detailing how experimental data will inform catalyst development and guide iterative improvements in reactor design.
- A description of the proposer's technical capabilities for fabricating the reactor.
- Identify risks associated with Phase 1a (Base), Phase 1b (Option) and Phase 2 (Option) and a risk mitigation plan with clearly defined risk metrics and success criteria.
- A staffing plan with relevant expertise to support Phase 1a (Base), Phase 1b (Option) and Phase 2 (Option) tasks in catalyst development and reactor design.
- Outline of the management approach to ensure the successful execution of the proposed effort.

HNO3 does not solicit:

- Approaches that proceed through an ammonia intermediate
- Approaches that use precursor chemicals other than air and water

Important Dates

BAA Released
December 1, 2025

Proposers Day
December 12, 2025

Abstracts Due, 4:00 p.m. Eastern
Encouraged, but not required
December 18, 2025

Abstract Feedback
January 5, 2026

FAQ Submission Deadline, 4:00 p.m. Eastern
January 26, 2026

Full Proposals Due, 4:00 p.m. Eastern
February 5, 2026

Tips for Successful Submission

- **Read the BAA carefully**
- Email questions to: **HNO3@darpa.mil**
- FAQ: https://www.darpa.mil/work-with-us/opportunities
- Form complete teams with comprehensive expertise & capabilities
  - Teaming is strongly encouraged
  - Teams should include a program coordinator/project manager (financial management experience is recommended)
  - There is no bias for teams internal to one institution or across multiple institutions, but effective communication and collaboration between team members is expected

HNO3: Transition and Impact at Program End

Two-Pronged Transition Plan focused on HNO_3 supply for downstream customers:

1) Defense industrial base
   - Partners may include DLA, Holston Army Ammunition Plant, defense contractors
2) Commercial market
   - Partners may include chemical industry, agricultural concerns, mining industry

50 L/day of 68% nitric acid

- Produce roughly 70 lb. of double-base propellant or RDX per day or 55 lbs of TNT per day
- With continuous production for a year: Fertilizer for 500 acres of wheat, 1250 acres of corn, or 2500 acres of potatoes
- Oxidizer in a solid-liquid split propellant rocket motor [SeREne-inspired]: 8-40 Hellfire-sized or 1-5 Sidewinder-sized missiles (dependent on formulation)

HBO uses 1-2% of the world's energy and 5% of the world's natural gas
What could we do with 175 TWh of spare energy?

RDX: Hexogen
TNT: Trinitrotoluene
DLA: Defense logistics agency
HBO: Haber-Bosch-Ostwald process
SeREne: Switchable reactive and energetics

www.darpa.mil