Novel routes and catalysts for synthesis of ammonia as alternative renewable fuel

Clustering event in Tokyo
キックオフミーティング

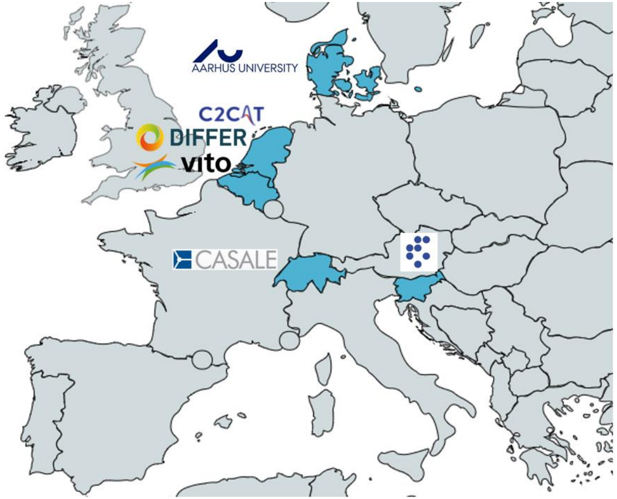
Introduction to ORACLE

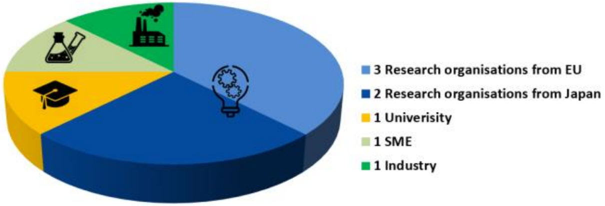
Online Presentation 22 November 2023

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101022738

ORACLE
三人寄れば文殊の知恵

THE PARTNERS





Partners & Responsibilities

WP1. Management and coordination (AARHUS UNIVERSITY)

WP2. Modelling and simulation
- i) atom scale
- ii) meso-scale
- iii) reactor-scale

(C2CAT, DIFFER, CASALE)

WP3. Thermo-catalytic reactor (benchmark)
- T3.1 Materials development
- T3.2 Reactor integration (C2CAT)
- T3.3 Reactor testing (VITO)

WP4. Electro-catalytic reactor
- T4.1 Materials development (C2CAT, ORIST)
- T4.2 Reactor integration (AARHUS UNIVERSITY)
- T4.3 Reactor testing (AIST)

WP5. Plasma-assisted electro-catalytic reactor
- T3.1 Materials development (C2CAT, ORIST)
- T3.2 Reactor integration (VITO)
- T3.3 Reactor testing (DIFFER, AIST)

WP6. Life-cycle assessment and techno-economic analysis (VITO, CASALE)

WP7. Dissemination, communication and exploitation (CASALE)

JST

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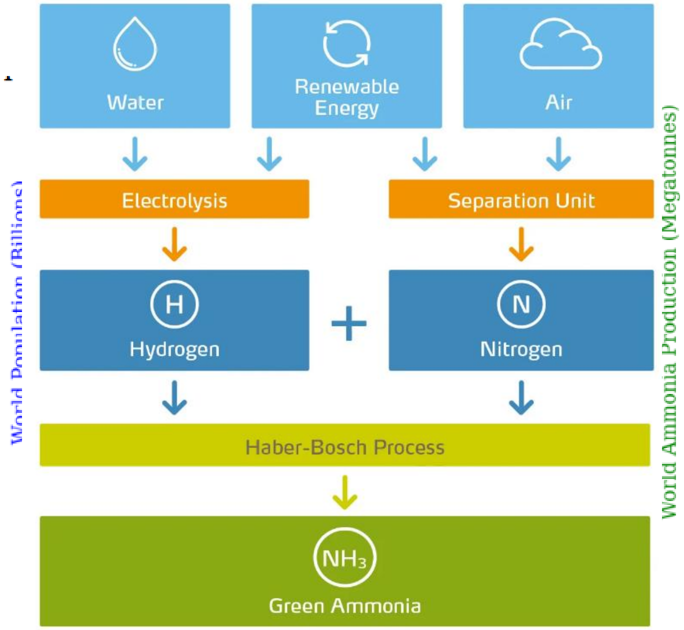
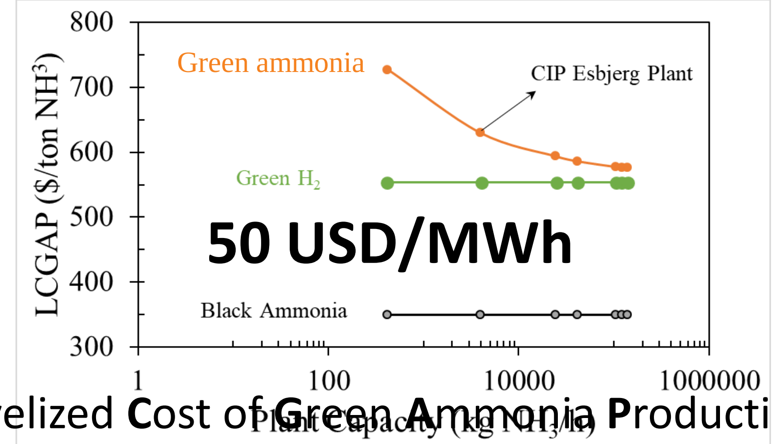
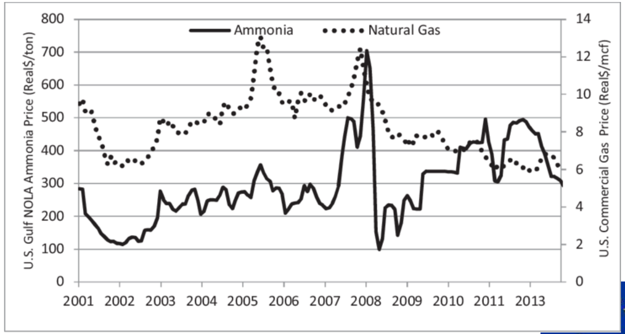
In the ORACLE project we want to electrify the ammonia production

Black ammonia solely responsible for 1-2% global CO_2 emissions!





Levelized Cost of Green Ammonia Production



Not for distribution

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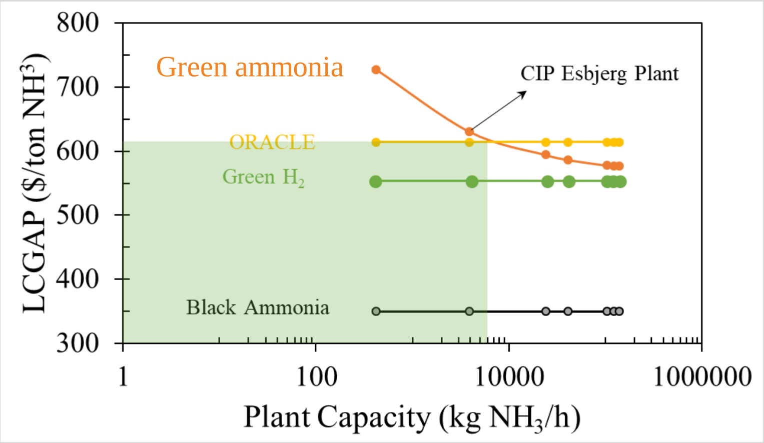
What is the scale of relevance of the technologies we look into in ORACLE?

- **Decentralised production of ammonia**
- Technology <1000 kg/h ammonia
- Ports, farms, islands



- ORACLE is NOT going to develop technology that can replace Haber-Bosch process at scales
- However, ORACLE technology is easier to deploy, smaller plants require smaller CAPEX, and LCGAP is not significantly higher than that of the conventional process at large scales

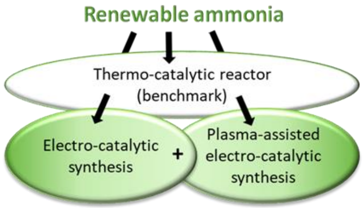


Figure 1.3 Schematic overview of the ORACLE project concept

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Potential market is larger farms, and energy storage applications

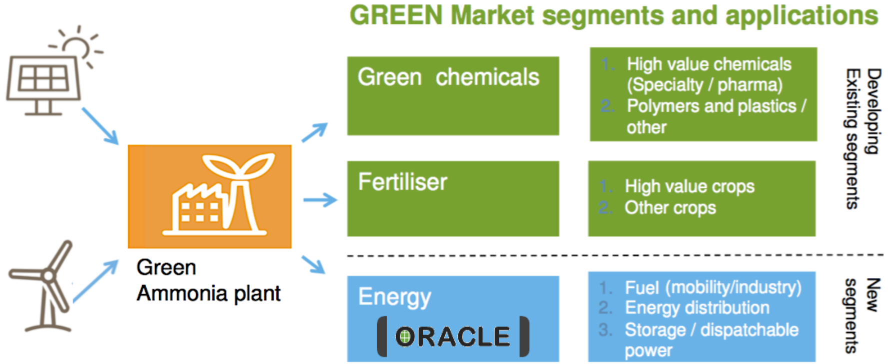

Figure 1.2. The ORACLE project's positioning in the new segments of green ammonia value chain, from deployment of renewable energy, through the use of ammonia as a renewable fuel, towards the desired low-carbon energy future for the European Union and beyond (figure adapted from Yara[1]).

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ORACLE

- TRL 1 – basic principles observed
- TRL 2 – technology concept formulated
- TRL 3 – experimental proof of concept
- TRL 4 – technology validated in lab
- TRL 5 – technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies)
- TRL 6 – technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies)
- TRL 7 – system prototype demonstration in operational environment
- TRL 8 – system complete and qualified
- TRL 9 – actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space)

We work to get to the TRL 3!

ORACLE runs in three streams to develop decentralised systems

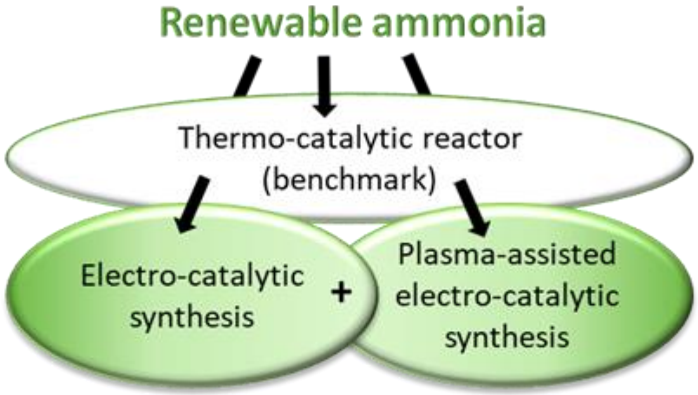

Figure 1.3 Schematic overview of the ORACLE project concept

$1/2N_2 + 3/2H_2 \leftrightarrow NH_3$ needs electrolyser

$1/2N_2 + 3/2H_2O \leftrightarrow NH_3 + 1/2O_2$

Is one electrolyser device, coupled to plasma or not

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Key performance indicators for ORACLE technologies

Table 2.2 Key Performance Indicators expected from ORACLE

Key Performance Indicators (KPI)	State-of-the-Art	ORACLE	Ultimate
TRL	1-2	3	high
Faradaic efficiency NH_3 [%]	Not validated	85	90
Faradaic eff NO [%]	Not validated	85	95
Energy Efficiency NH_3 [MWh/ton]	60	10	<10
Energy Efficiency NO [MJ/mol N]	2700	1300	50
NH_3 formation rates [mol/s cm^2]	0.45×10^{-8}	2×10^{-8}	40×10^{-8}
Ramp-up time (hrs)	days	minutes	seconds
Use of critical or noble materials	various	none	none

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Electrified thermocatalytic reactor

- Induction heated catalyst in the reactor
- Fast heating, small heat losses
- Direct heating of the catalyst
- Fully electrified reactor-dynamic operation

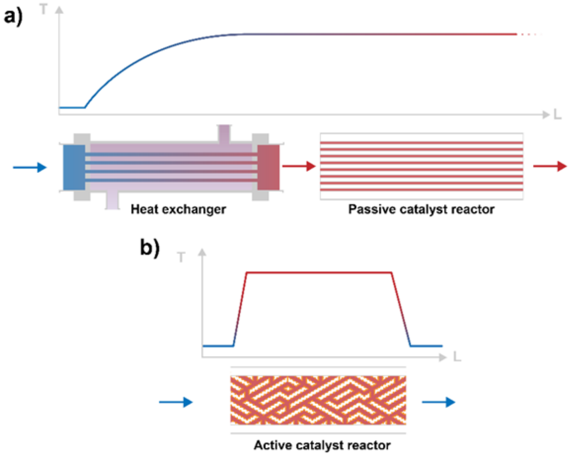

Figure 1.4 Schematic representation of (a) convectional catalytic reactor setup coupled with heat exchanger unit to preheat hydrogen/ammonia before reaching the passive catalyst reactor, and (b) the AC-mediated heating reactor set-up, where the active catalyst material is deployed on the catalyst support containing magnetic nanoparticles.

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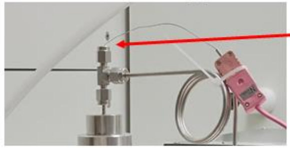
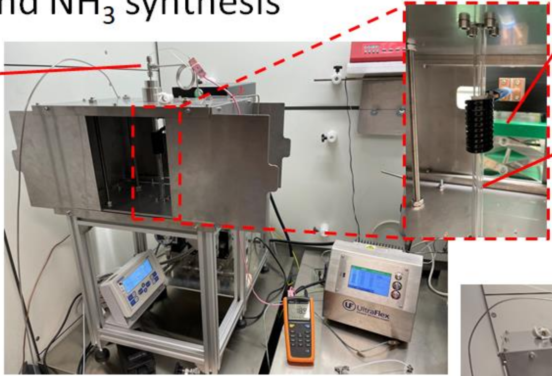
Electrified thermocatalytic reactor – key results so far

Setup for magnetic heating measurements and NH_3 synthesis

Thermocouple N-type

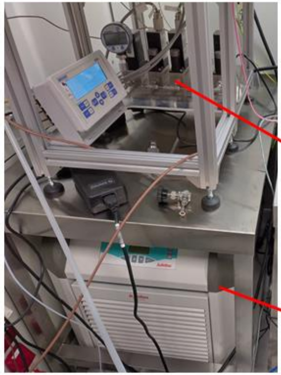




Copper tube (9 turns, 17 mm inner diameter, 29 nm outer diameter, 56 nm height, 235 kHz)

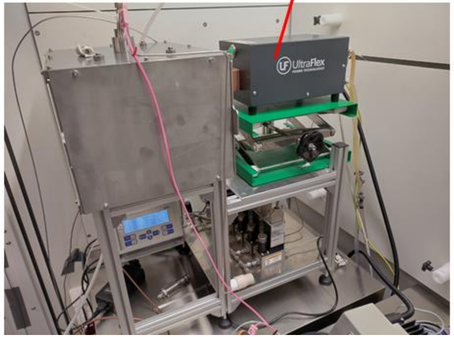
Quartz reactor tube (9 mm inner diameter, 360 mm length)

High-frequency generator (Ultraflex HS-4W)



Mass flow controllers

Compressor cooler, Julabo FL1701



Designed, assembled and tested.

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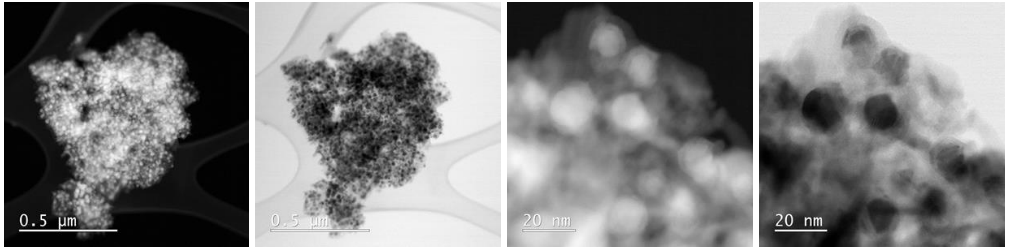
Electrified thermocatalytic reactor – key results so far

Catalyst Nanocomposite: XXYY alloyed nanoparticles in alumina matrix

This benchmarks very well to the literature, and we use no promotors (alkali metals) at the moment.

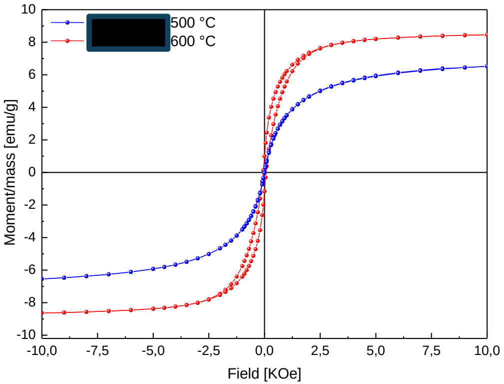


JST

vito

C2CAT

Successful scale-up of synthesis to 18 g of precursor per batch



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Electrocatalytic concept at room temperature

- Possibly neat process, but currently plagued by false positive measurements
- Seems wrong catalysts in use so far
- However, if correct catalyst are identified and experimental setup designed such that the cathode favours nitrogen adsorption, one can fixate N_2 and H_2O at cost around 10000 kWh/ton NH_3, comparable to HBR
- Japanese partners are involved and they develop water oxidation catalysts in HER supressing electrolytes

SELECTIVITY ISSUE, cathode produces hydrogen ammonia

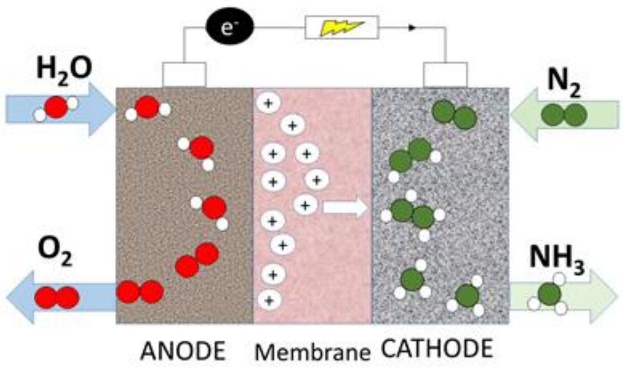

Figure 1.8 The electrocatalytic concept.

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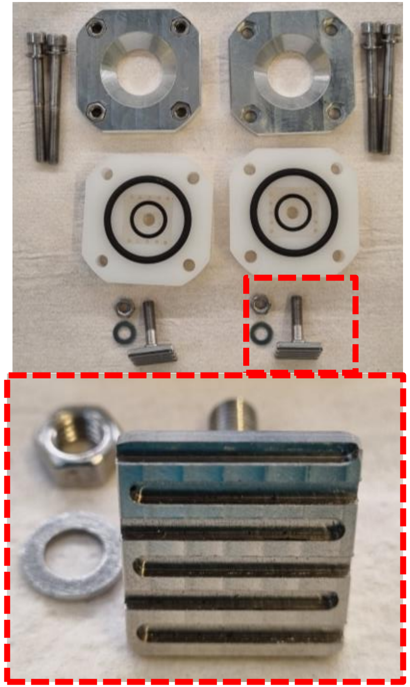
Key results- electrocatalytic reactor – used for aqueous systems



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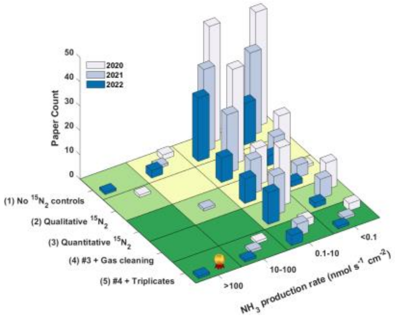
Key results – electrocatalytic ammonia

- **In 2.5 years we could not get any ammonia when proper laboratory procedures used and clean setup.**
- We looked and made a review in the literature, and we got discouraged to work further in aqueous media. High reliability papers synthesize about 30 microgram per batch and this is too small amount and margin of error too high for us to take risk with water media.
- **Now we switch from water media to non-aqueous media which are more stable in negative region**



RESEARCH ARTICLE
Energy Technology
www.entechnol.de

Low-Temperature Electrochemical Ammonia Synthesis: Measurement Reliability and Comparison to Haber–Bosch in Terms of Energy Efficiency

*Fateme Rezaie, Søren Læsaa, Nihat Ege Sahin, Jacopo Catalano, and Emil Draževič**

Electrochemical nitrogen reduction reaction over gallium – a computational and experimental study†

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SELECTIVITY ISSUE, cathode produces hydrogen and NOT ammonia

Seems to be related to water instability and large overpotentials needed for nitrogen reduction.

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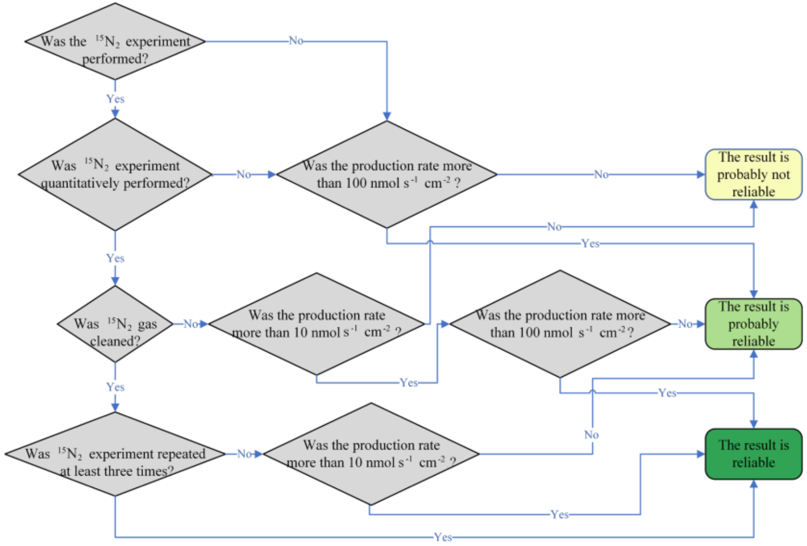
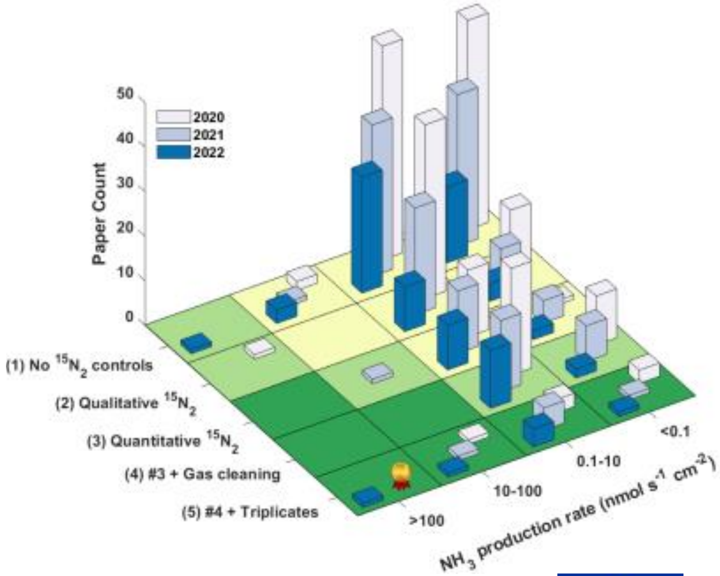
On the review of papers.

We were worried if we are at the right path. We developed rigorous approach to evaluate literature and identified successful approaches in aqueous media. We reviewed around 500 papers using our approach.





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Plasma-assisted electro-catalytic route

- Plasma breaks nitrogen triple bond
- Nitrogen is very reactive as single atom
- Easy to reduce N to NH_3, once triple bond is broken
- Here two concepts:

1) N_2 to 2N to NH_3
2) N_2 to $2NO_x$ to NH_3

Here Japanese partners develop hydrogen evolution reaction catalysts.

Advantage: Highly-selective reduction of nitrogen, as nitrogen is plasma-activated

Possible drawback: Needs to be engineered so that the energy consumption is minimal.

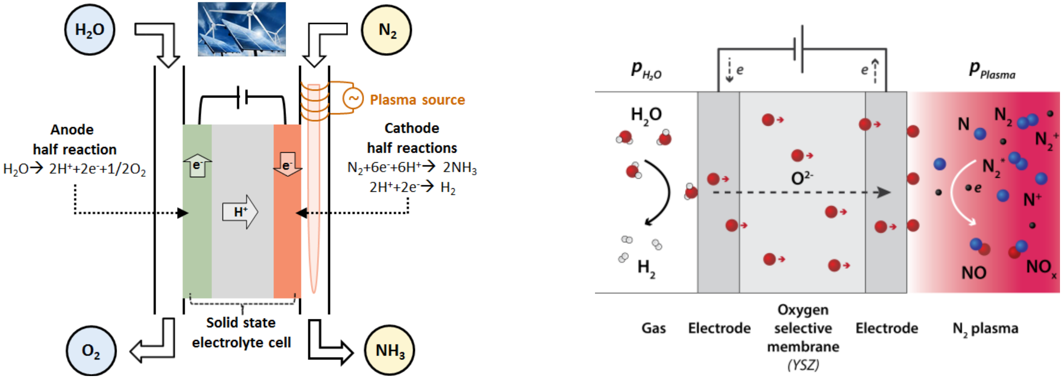

Figure 1.11 A) Plasma aided electrochemical synthesis of ammonia from water and nitrogen. The fuel electrode (cathode) is exposed to plasma activated atomic nitrogen reacting with protons transmitted by the electrolyte and derived from water electrolysis. **B)** Schematic of plasma activated electrolysis of Water and Nitrogen for the production of Nitric Oxide and Hydrogen, driven by renewable electricity.

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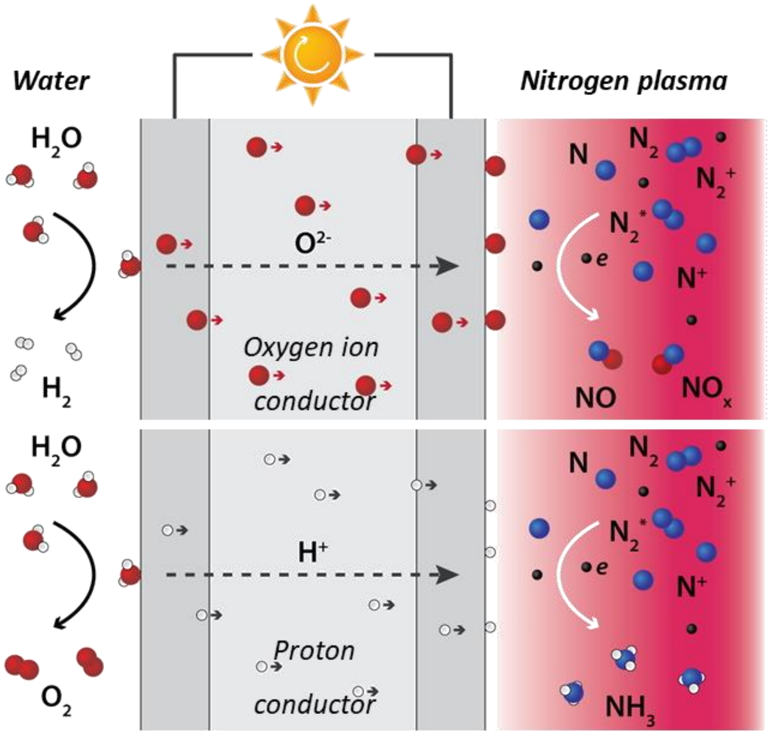
Key results plasma-assisted electro-catalytic route



H. Patel et al, ACS Energy Letters, 2019
R. Sharma et al, ACS Energy Letters, 2021

Nitric oxide synthesis

- *Up to 93% Faradaic efficiency to NO*
- *Maximum rate 63 nmol NO per s*
- *NO concentration > 10^3 times equilibrium*
- *1350 MJ/N-mol (Literature: 50-2700 MJ/N-mol)*

Ammonia synthesis

- *Up to 88% Faradaic efficiency to NH_3*
- *Maximum rate 26.8 nmol NH_3 per s*
- *NH_3 concentration > 10^4 times equilibrium*
- *605 MJ/N-mol (Literature: 50-2700 MJ/N-mol)*

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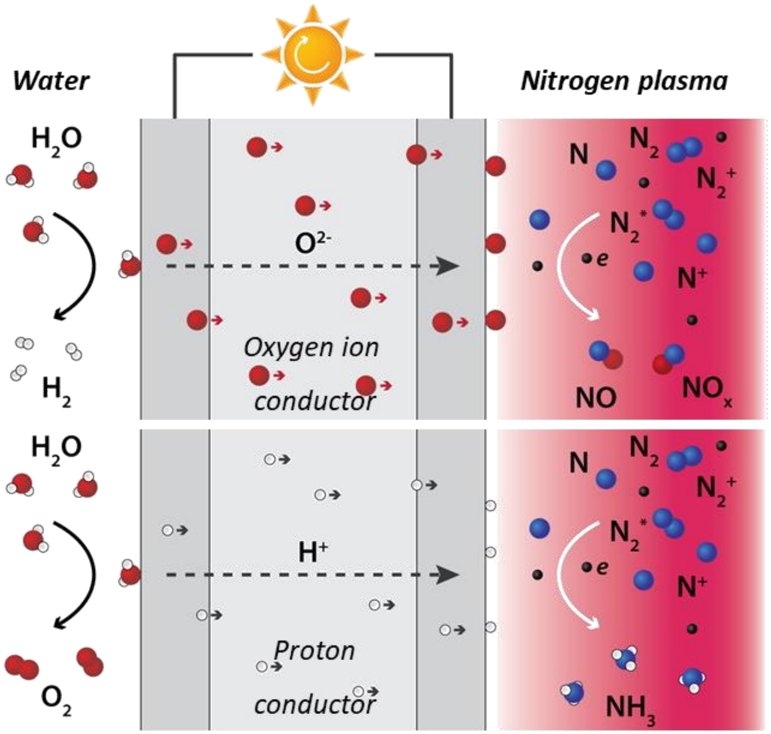
Key results plasma-assisted electro-catalytic route



H. Patel et al, ACS Energy Letters, 2019
R. Sharma et al, ACS Energy Letters, 2021

Challenges

- *Increase productivity*
- *Decrease energy consumption*
- *Understanding*

Directions

- *Match plasma fluxes with catalyst TOF*
- *Develop materials and electrode architectures*
- *Plasma diagnostics → clarify active species*
- *Modeling…*

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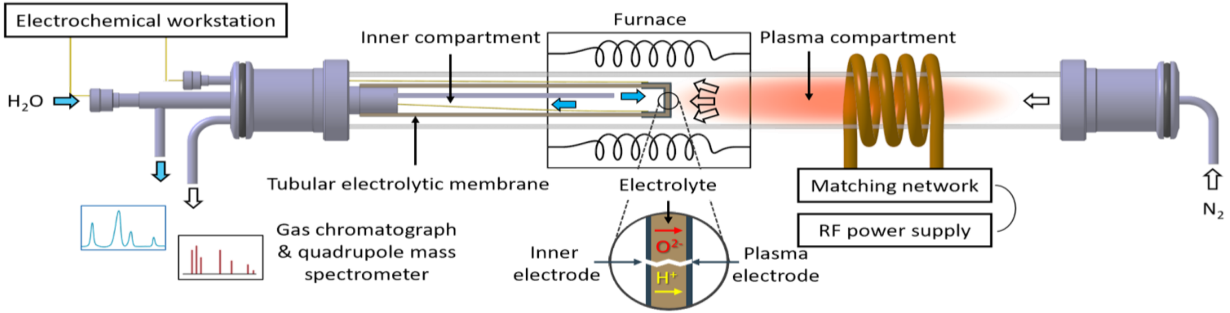
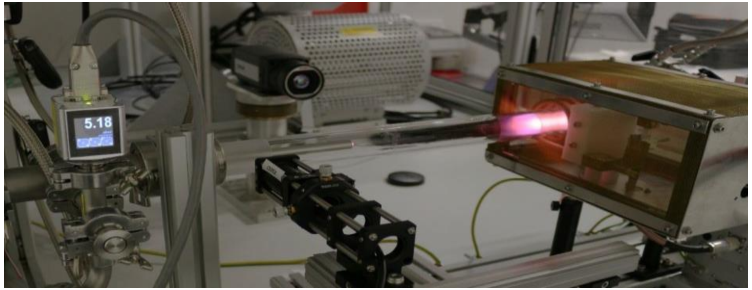
Key results plasma-assisted electro-catalytic route





Reactor and cell integration

- Upgrading existing reactor
  - Design & modification (see D5.2)
- Setup duplication
  - Plasma diagnostics: Radical probe
  - Separation of NO vs NH_3 experiments

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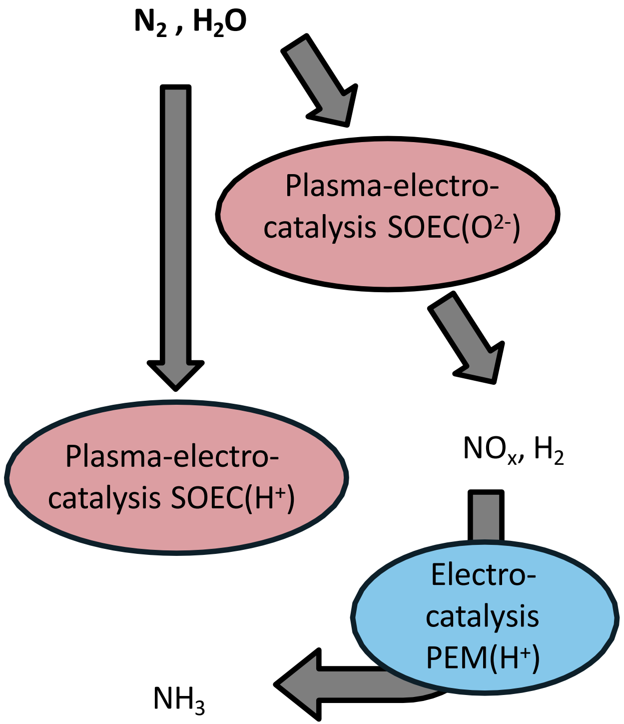
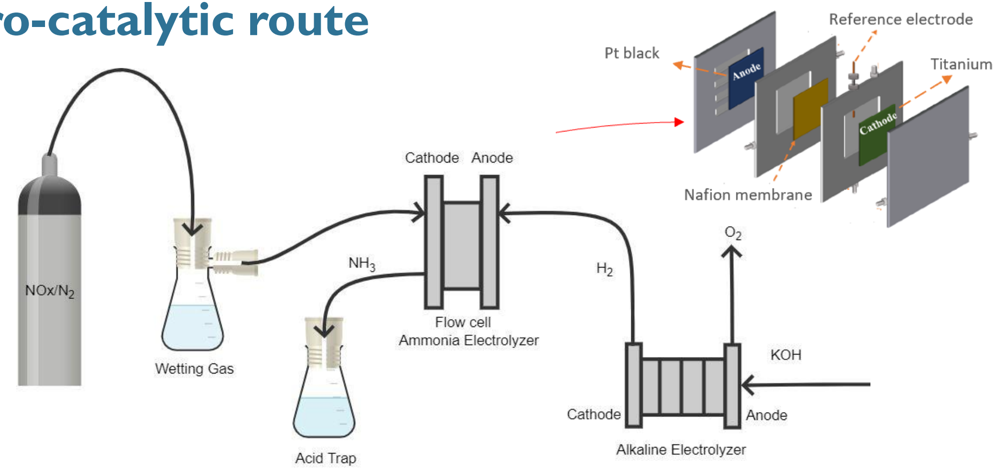
Key results plasma-assisted electro-catalytic route





- Reactor,gases and materials are purchased.
- Anode:Pt paper
- Cathode:Ti mesh
- Operation:NOx will be fed in the cathode and H_2 in the anode

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THANK YOU

ありがとうございました

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