Ammonia as hydrogen carrier and carbon-free fuel

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Role of ammonia in a net-zero hydrogen economy

The limitations of hydrogen

Challenges in hydrogen storage and transportation

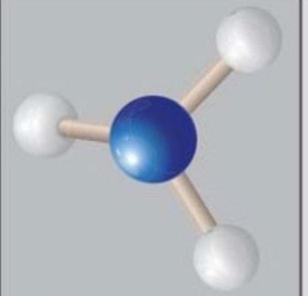
Production and sourcing of hydrogen

Safety concerns due to high flammability

Role of ammonia in a net-zero hydrogen economy

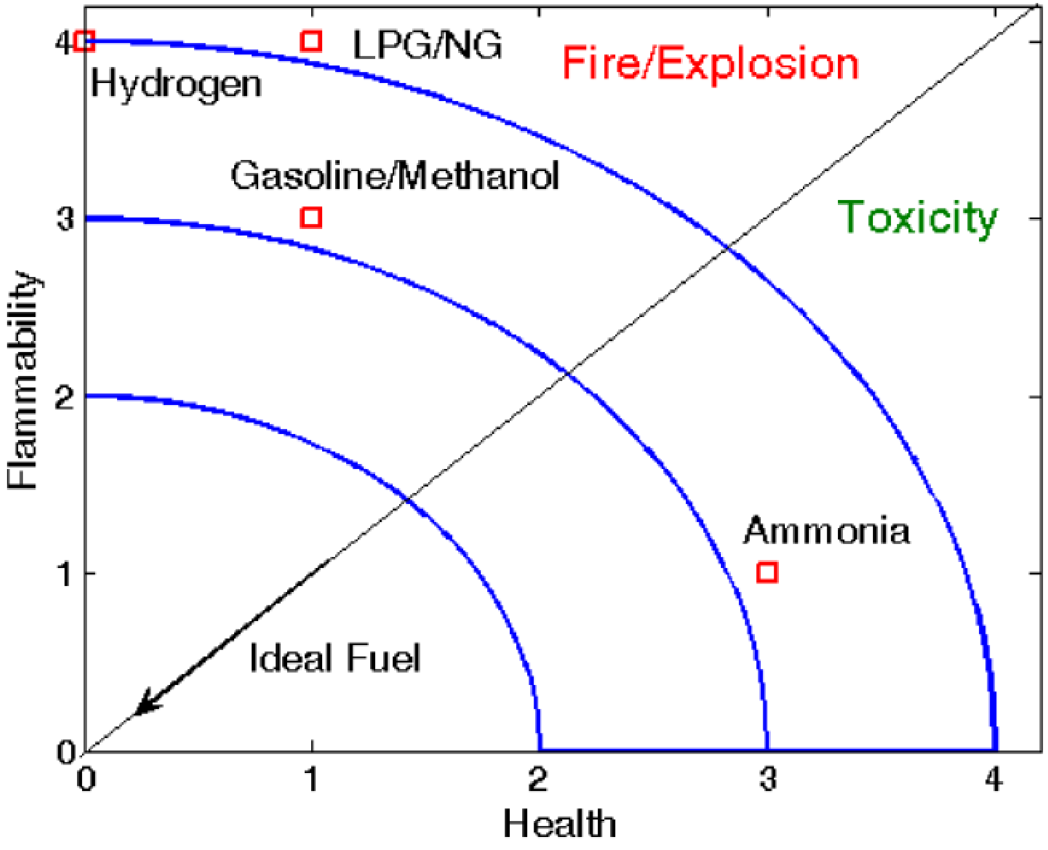
Ammonia to the rescue?

- **Carbon-free hydrogen carrier** with a high hydrogen content of 18%.
- Higher volumetric energy density, smaller flammability range, easier leak detection due to strong smell.
- **Ease of storage and transportation**: liquid hydrogen (pressure ~700 bar, or below -253 °C) vs. liquid ammonia (~10 bar or lower when below -33 °C).
- **Established production method** (Haber-Bosch process) and can be adapted to use green hydrogen.
- **Existing infrastructure** and global networks for ammonia production, distribution, and storage.

	 HYDROGEN, H_2	 AMMONIA, NH_3
Volumetric energy density (MJ/L)	$10_{(l)}$, $6_{(g,\ 700\ bar)}$	$14_{(l)}$
Gravimetric energy density (MJ/kg)	142	23
Flammability limit (Equivalence ratio)	0.10–7.1	0.63–1.40
*Flammability hazard**	4	1
*Health hazard**	0	3

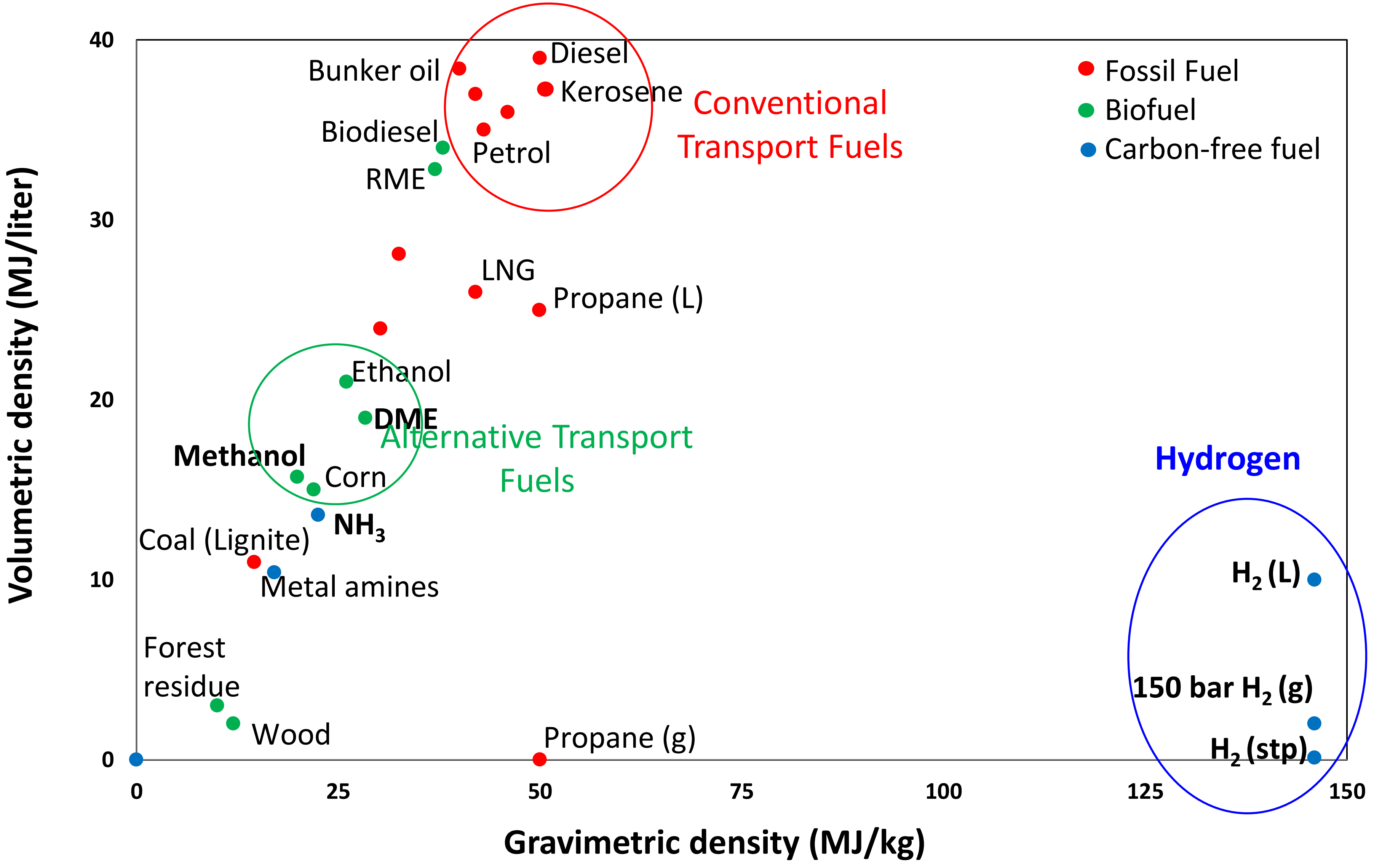
https://www.thechemicalengineer.com/features/h2-and-nh3-the-perfect-marriage-in-a-carbon-free-society/

Safety

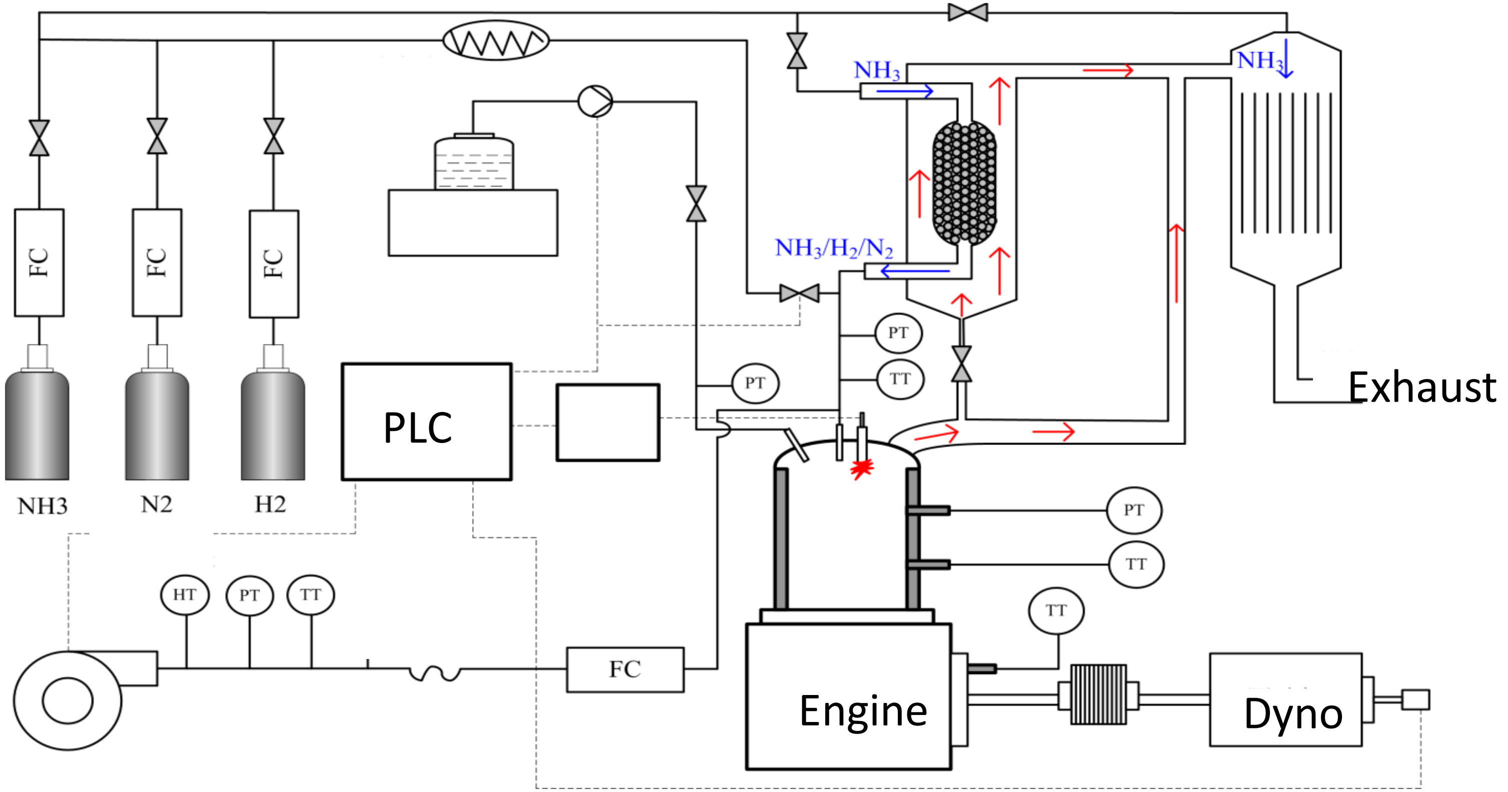


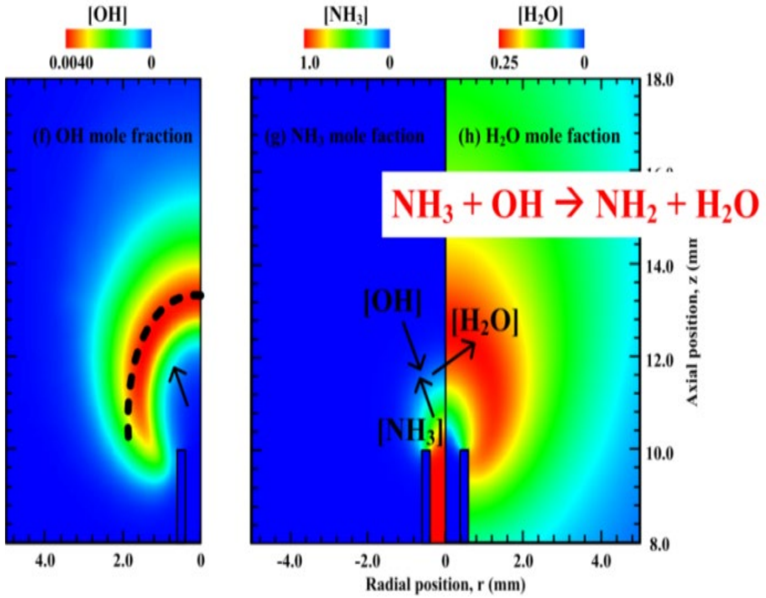
- Extensive knowledge base in production, transportation and storage of ammonia, design of ammonia system/materials, safe handling and emergency procedures
- U.S. Occupational Safety and Health Administration (OSHA) has set a 15-minute exposure limit for gaseous ammonia of 35 ppm by volume in ambient air
- Ammonia vapor has a sharp pungent odour that acts as a warning for potentially dangerous exposure. The average odour threshold is 5 ppm, which is well below any danger or damage.
- Excellent data base for ammonia related accidents showing great safety record, safer than any other fuels

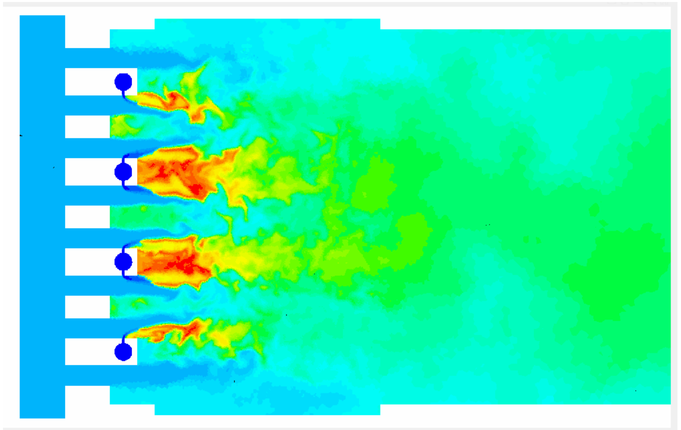
Energy Density Matters



NH_3 in Internal Combustion Engines





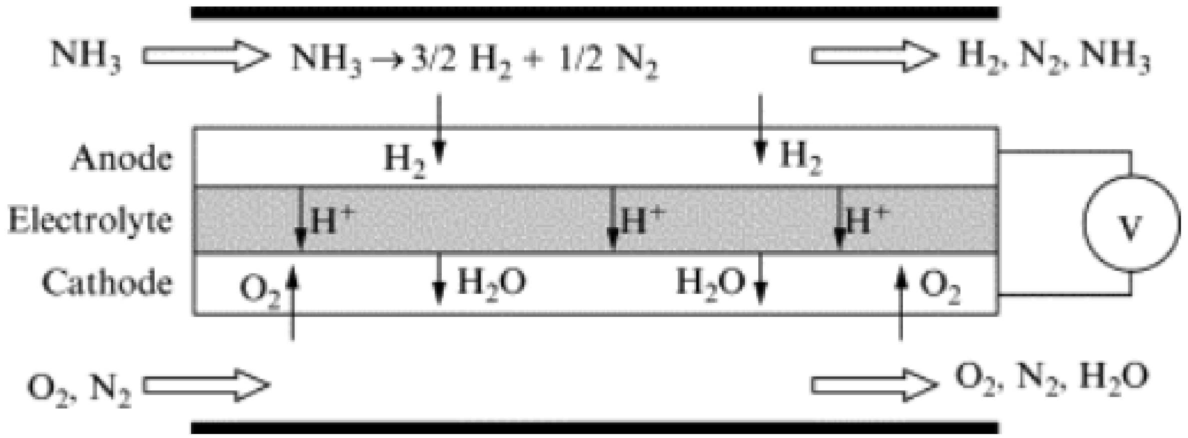


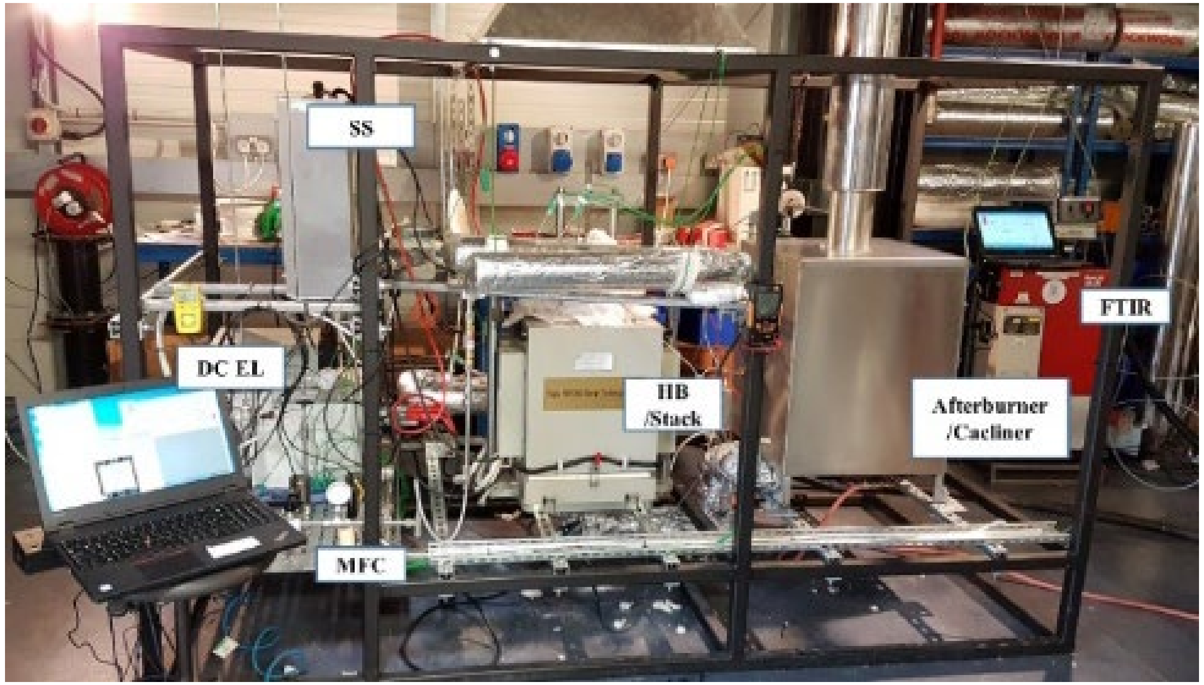
1. Lesmana, H., **Zhu, M**; Zhang, Z., Gao. J., Wu, J, and Zhang, D. 2022, *Combustion & Flame,* 241, 112053
2. Lesmana, H., **Zhu, M.**, Zhang, Z., Gao. J., Wu, J, and Zhang, D. 2021, *Proceedings of the Combustion Institute*, 38(2), 2023-2030
3. Lesmana, H., **Zhu, M**; Zhang, Z., Gao. J., Wu, J, and Zhang, D. 2020, *Fuel,* 278, 118428

Ammonia-related work at Cranfield University

- Ammonia solid oxide fuel cell
- Electrochemical ammonia cracking
- Catalytic ammonia combustion
- …

NH_3 Solid Oxide Fuel Cell





5 kW SOFC system at Cranfield

- Same configuration of H_2 SOFC
- Direct power generation without NOx
- Handle low concentration of ammonia
- Challenges are the catalyst stability

Ammonia Electrochemical Cracking

General Description

Anode: $2NH_3 + 6OH^- \longrightarrow N_2 + 6H_2O + 6e^-$

$E(vs\ \text{SHE}) = -0.77\ \text{V}$

Cathode : $6H_2O + 6e^- \longrightarrow 3H_2 + 6OH^-$

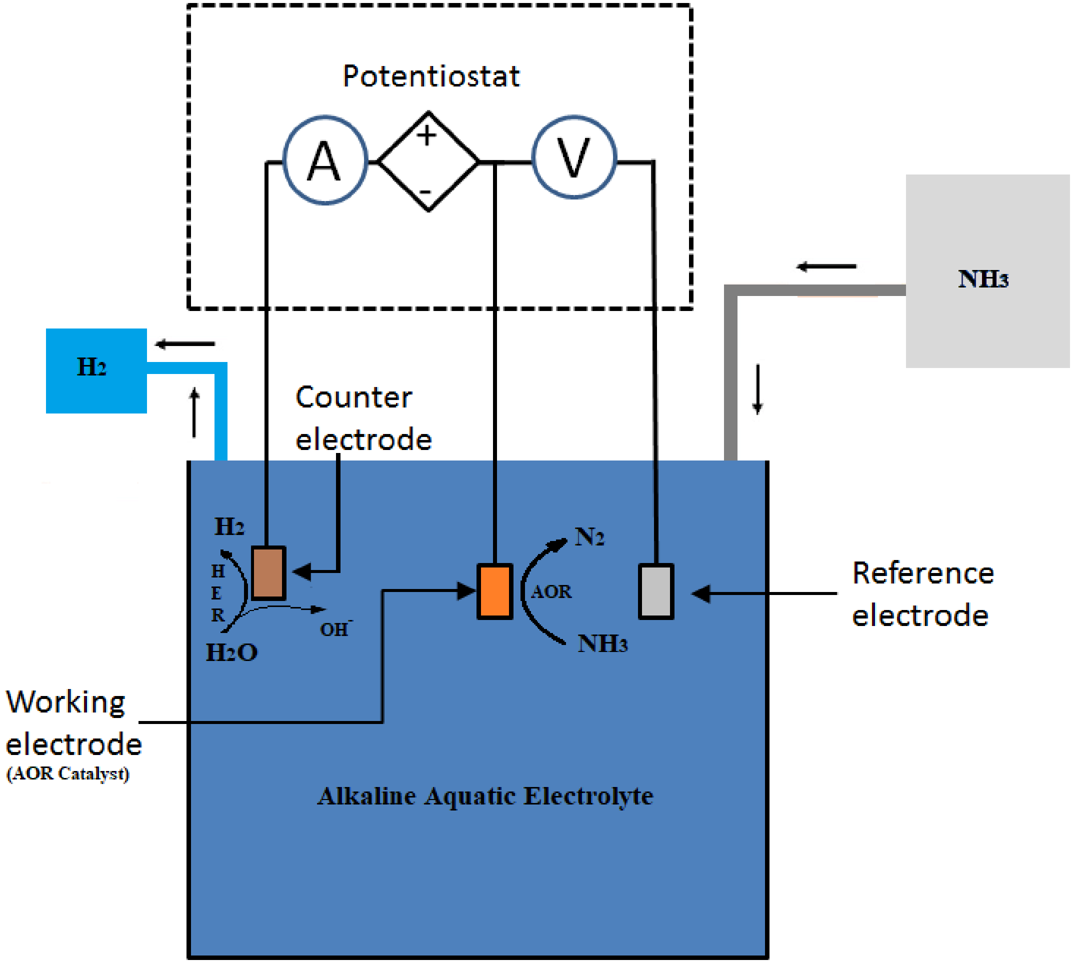
$E(vs\ \text{SHE}) = -0.83\ \text{V}$

Total : $2NH_3 \longrightarrow N_2 + 3H_2$

$E = 0.06\ \text{V}$

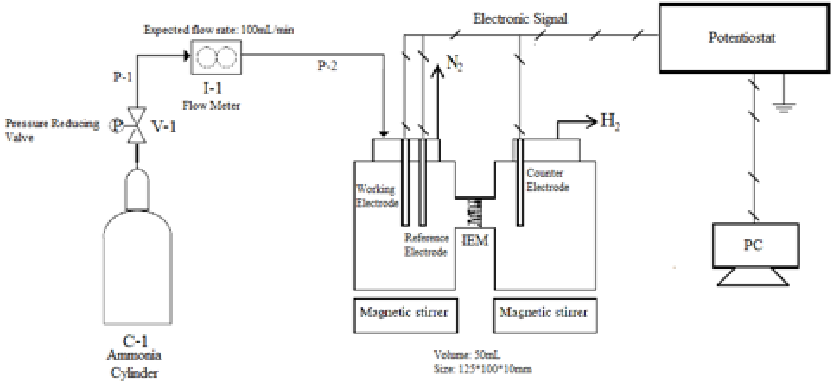
$E_{H_2O} = 1.23V$

- Theoretical energy consumption is 95% lower than water electrolysis
  - AOR: $1.55 wh/gH_2$
  - HER: $33 wh/gH_2$

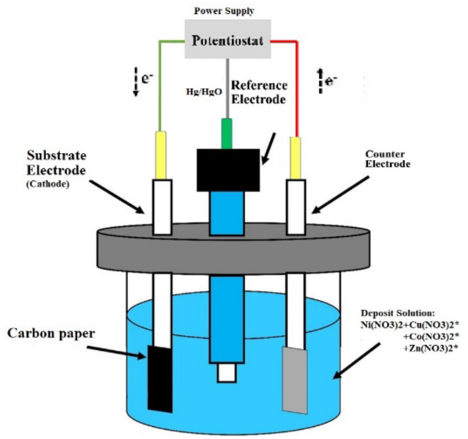


Schematic Diagram of Ammonia Electrochemical Cracking

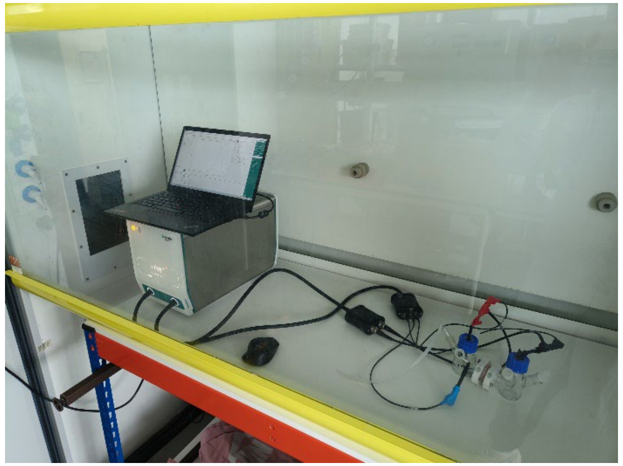
Electrochemical Cracking of Ammonia

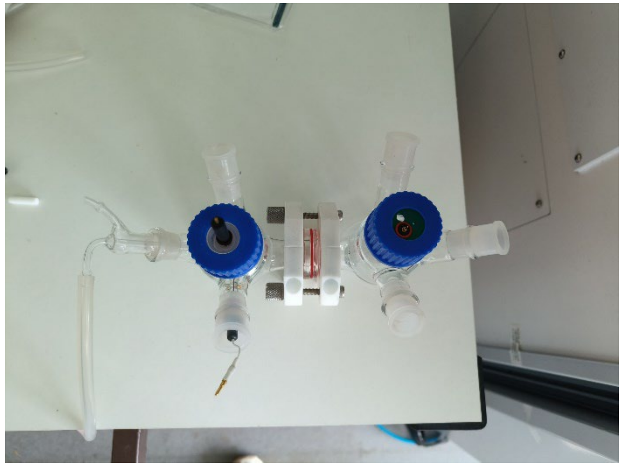


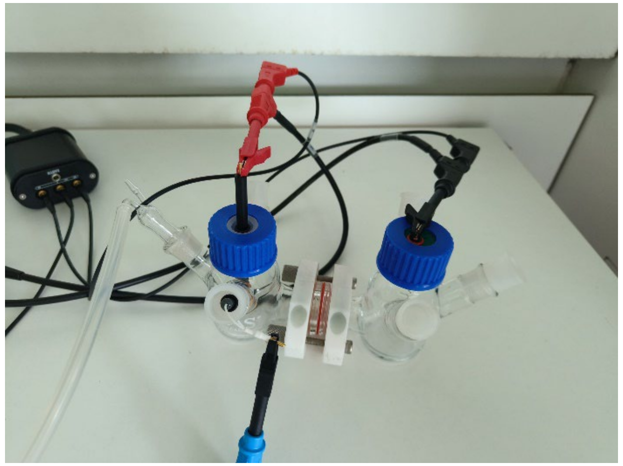
Schematic Diagram of Electrochemical Reactor



Schematic Diagram of Electrodeposition Reactor







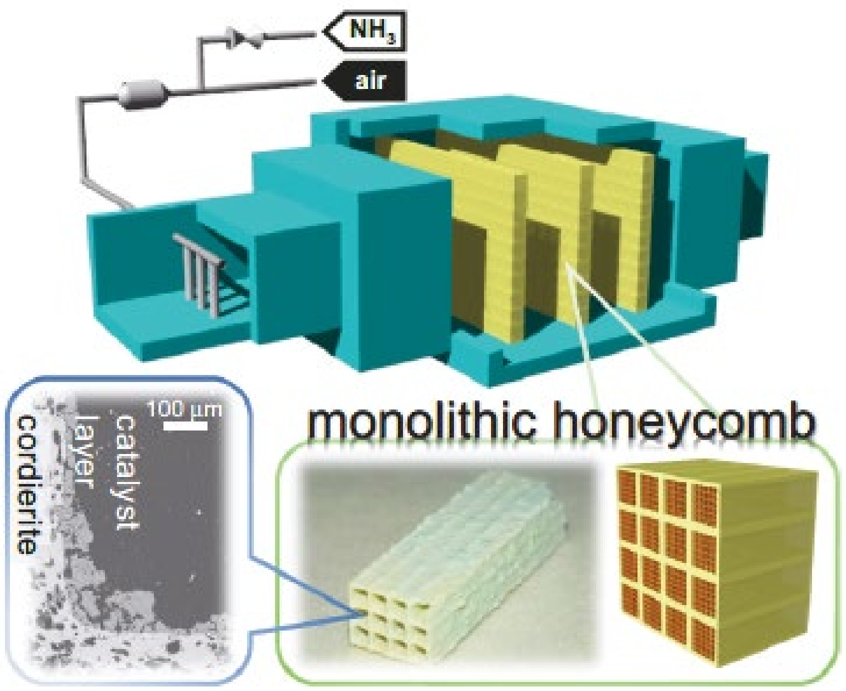
Ammonia source options:

- First phase: 0.1M $NH_3 \cdot H_2O$
  (For rapid screening samples)
- Second phase: Ammonia gas pipeline system
  (For more detailed testing of samples' electrochemical performance)

(Supported by EPSRC and EDF)

Catalytic ammonia combustion

- Pt- and Pd-based catalysts widely used for catalytic ammonia oxidation processes (e.g. treating low-concentration NH_3 as a pollutant, converting NH_3 to NO for nitric acid production)
- Existing research on ammonia combustion catalysts:
  - CuO-based catalysts supported on ceramic materials.
  - Noble metal-based catalysts, e.g. Pt/Al_2O_3.
  - Bimetallic catalysts, e.g. supported Cu-Ag, Cu-Ru catalysts.
  - Structured catalysts.



Honeycomb CuO-Al_2O_3 catalyst. Ammonia Combustion Properties of Copper Oxides-based Honeycomb and Granular Catalysts (jst.go.jp)

CuO-based catalysts with different support materials

(Supported by EPSRC)

Numerical simulations – DFT-based calculations

- **Density Functional Theory (DFT):**
  - A computational quantum mechanical modelling method used to investigate the electronic structure of atoms, molecules, and solids.
- **Application of DFT in catalysis:**
  - Interaction between catalysts and reactants at an atomic level.
  - Active sites identification.
  - Reaction pathway identification.
  - Widely applied in hydrogen-related studies for catalyst development [1,2]

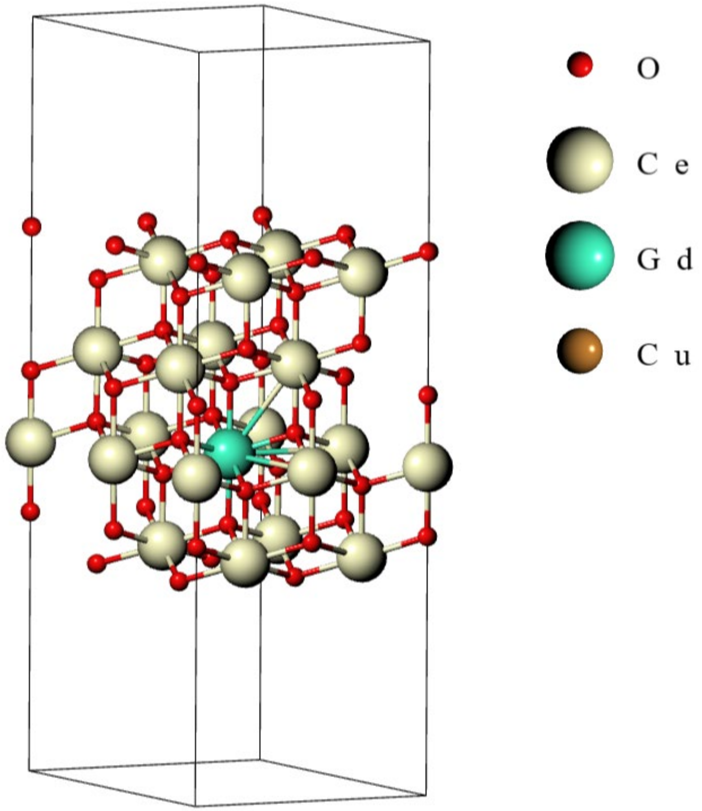
[1] Wang S, Nabavi SA, Clough PT. A review on bi/polymetallic catalysts for steam methane reforming. Int J Hydrogen Energy 2023;48:15879–93. https://doi.org/10.1016/j.ijhydene.2023.01.034
[2] Wang S, Shen Z, Osatiashtiani A, Nabavi A, Clough P. Ni-Based Bimetallic Catalysts for Hydrogen Production Via (Sorption-Enhanced) Steam Methane Reforming. https://doi.org/10.1016/j.cej.2024.150170

DFT-based calculations: Model construction

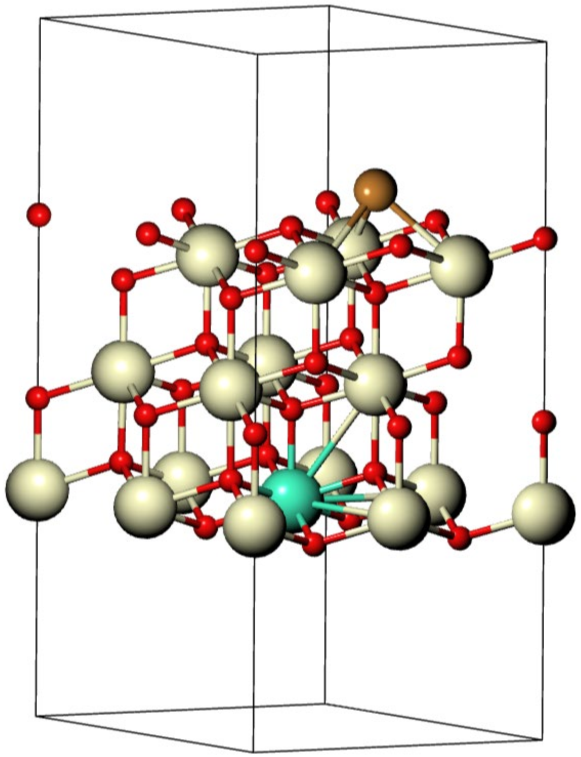
- Slab models are used to simulate the surface, bulk structure, and reaction environment of the catalysts under real-life conditions.

Top layers relaxed to simulate surface reconstruction

Bottom layers fixed to simulate bulk structure of the catalyst



GDC slab model

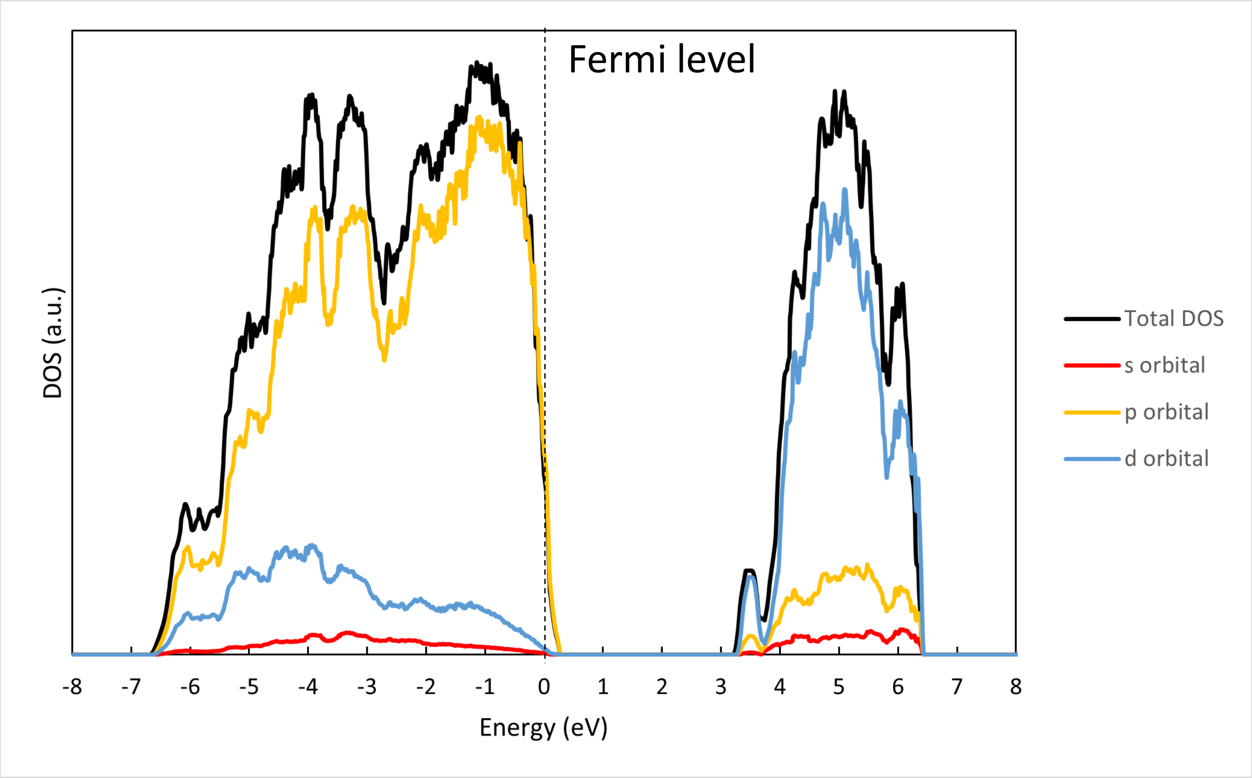


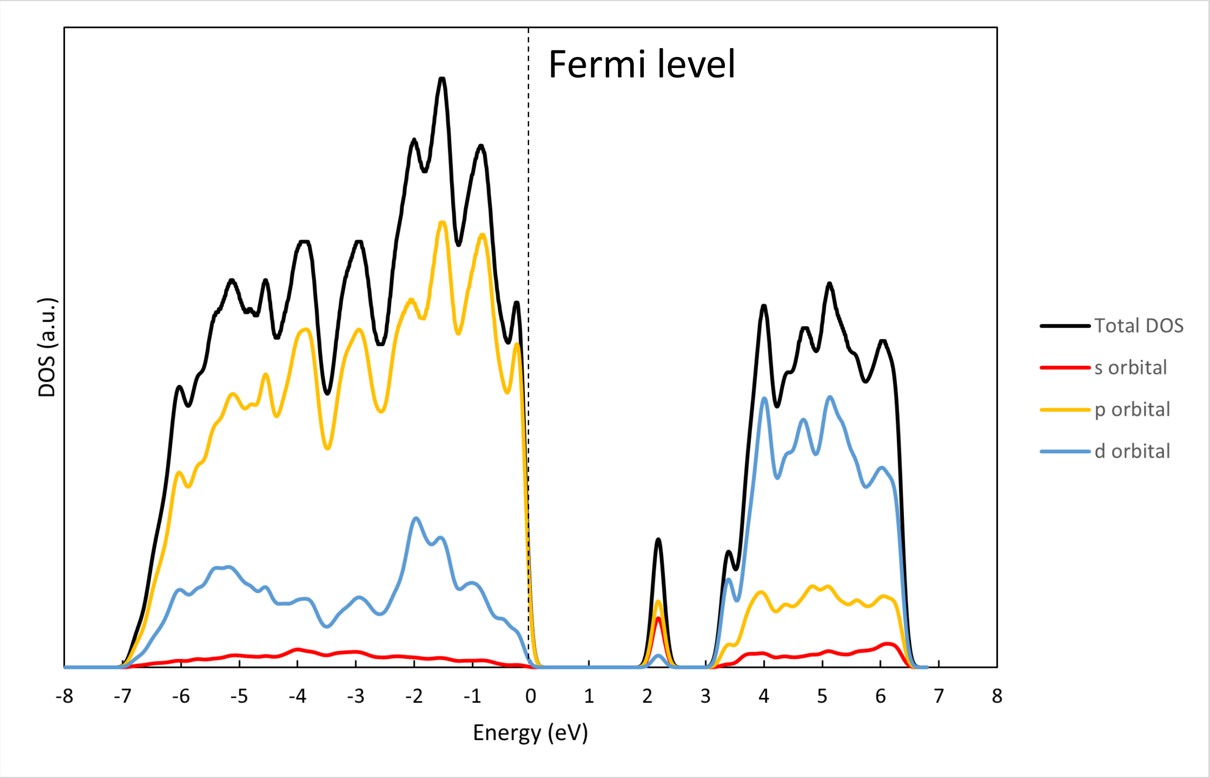
Doping of Cu and Ge atoms to achieve the desired molar ratios

CuO-GDC slab model

DFT-based calculations: Results

Density of States (DOS) of YSZ (left) and CuO-YSZ (right)

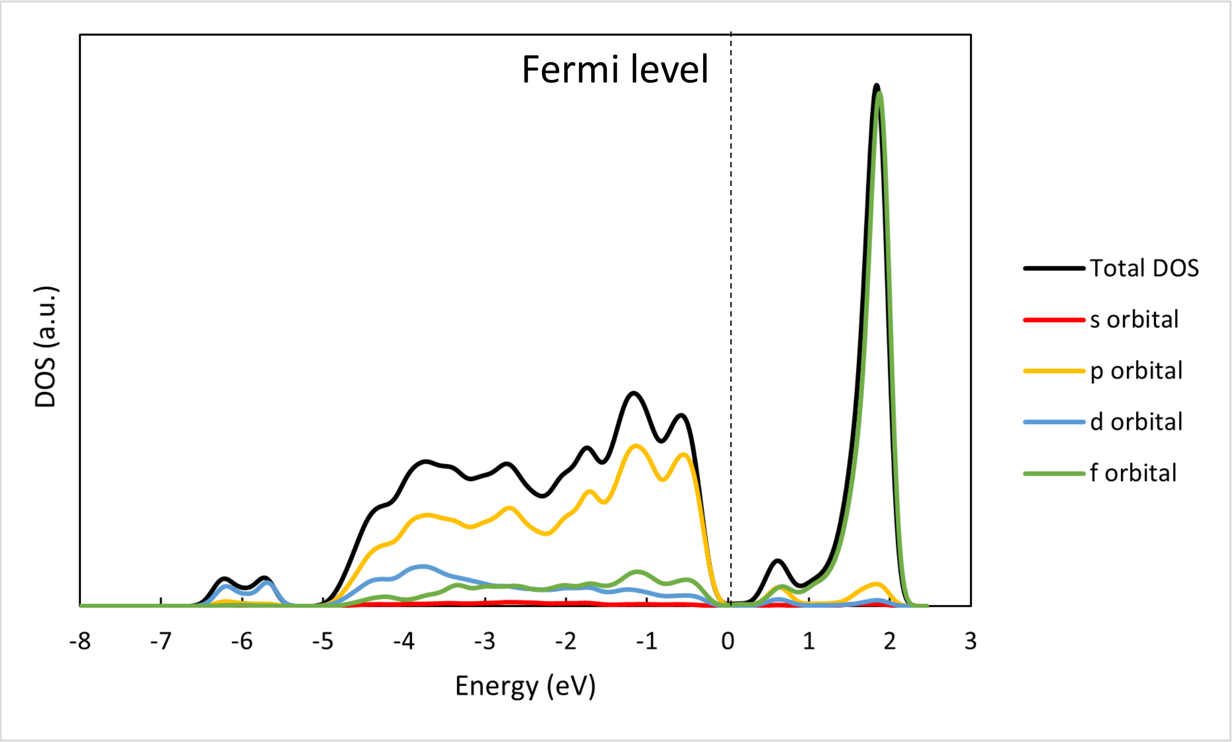


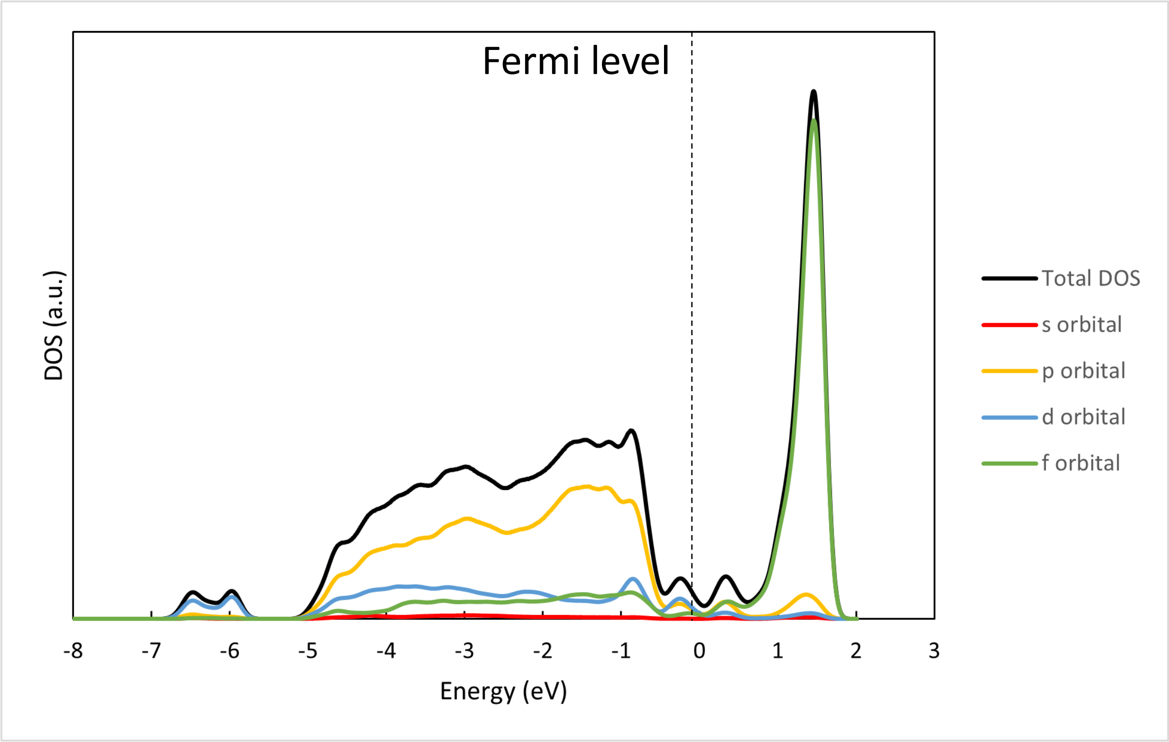


- Smaller band gap → increased electronic conductivity.
- More states near the fermi level → better electron transfer between the catalyst and the reactants, which can enhance catalytic activity.

DFT-based calculations: Results (cont.)

Density of States (DOS) of GDC (left) and CuO-GDC (right)





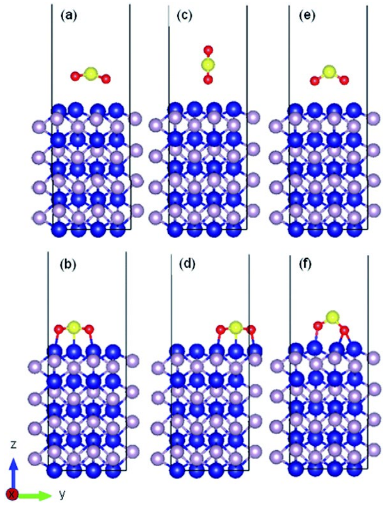
- Smaller band gap compared with CuO-YSZ, no band gap near the fermi level → high electronic conductivity.
- More states near the fermi level → better electron transfer between the catalyst and the reactants, which can enhance catalytic activity.

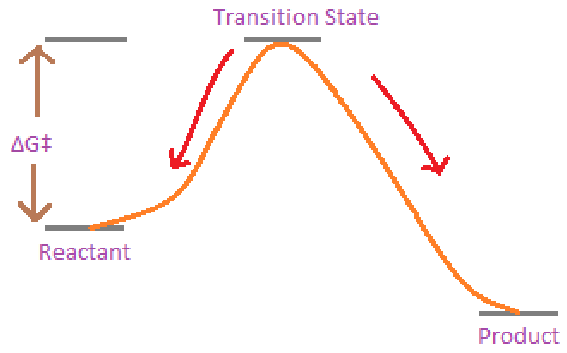
Numerical simulations – next steps and wider application

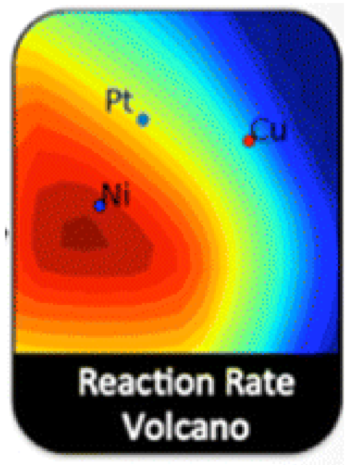
- **Adsorption energy**: calculate adsorption energies of reactant and product species, investigate interaction between N and O atoms (or other key species) with the catalyst surface.

- **Reaction energy barrier**: identify reaction pathway and calculate activation energy for key reaction steps.

- **Microkinetic Modelling**: link catalytic activity of a given material with the adsorption energies of key species in the reaction system.





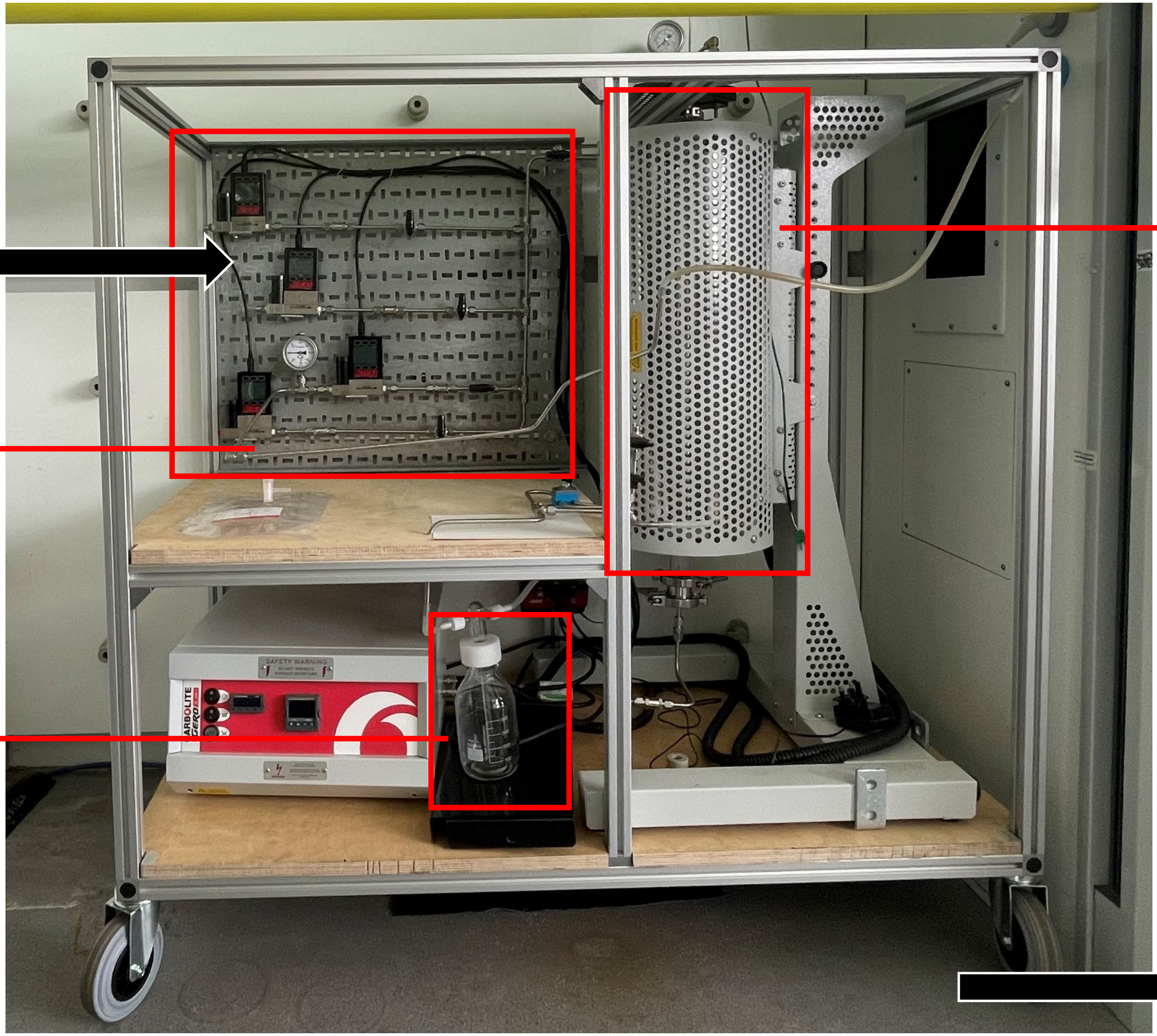


Experimental design and setup

Inlet gas composition: NH_3, O_2, and Ar

Mass flow controllers for inlet gas flow rate regulation

Acid trap for ammonia measurement



Tube furnace and quartz reactor

Outlet gas composition measured by GC-TCD and gas analysers

Experimental – next steps and wider application

- Next steps:
  - Carry out ammonia combustion tests to evaluate the effect of different support materials and bimetallic catalysts on the activity and selectivity of the catalysts.

- Other applications include but are not limited to:
  - Ammonia thermal cracking for hydrogen production
  - Ammonia-hydrogen dual-fuel combustion
  - Methane cracking or reforming for hydrogen production

Thank you for your attention.

Any questions?

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