질소 순환 시스템 및 관련 소재
Nitrogen Cycle System and Related Materials

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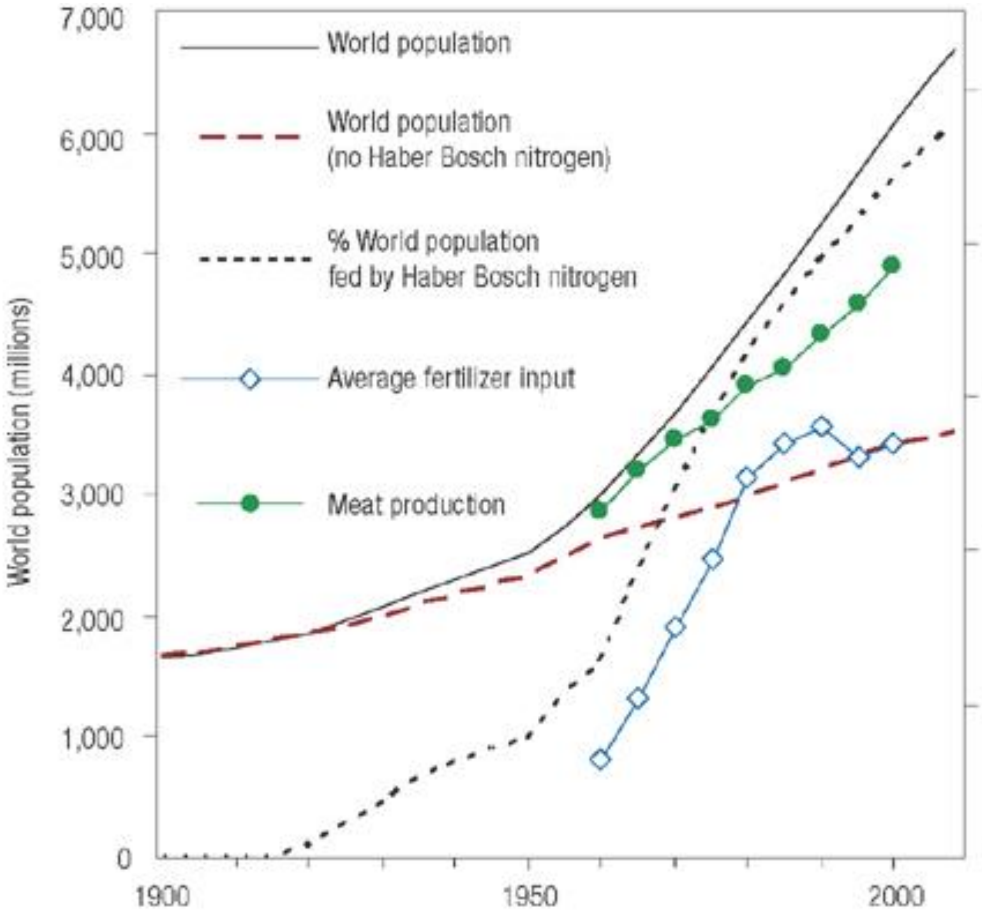
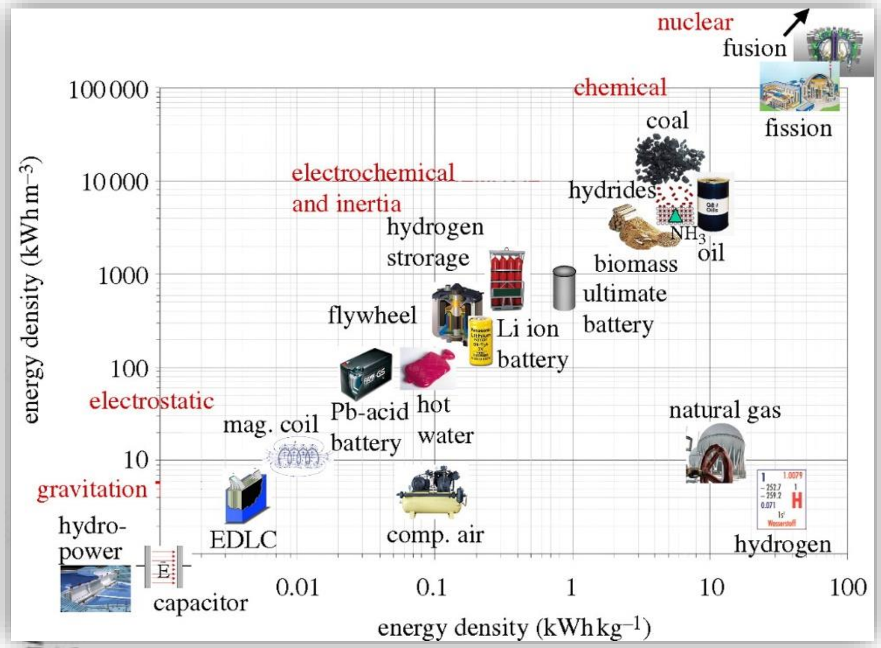
Ammonia (NH_3)

- Colorless gas with a pungent smell, lighter than air (0.589) / m.p.(-77.7 °C), b.p.(-33.3 °C)
- **Fertilizer** (88% of NH_3 is used), Explosives, Textiles, Precursors to nitrogenous compounds, Cleaner, Fermentation, and Antimicrobial agent for food products, …
- Emerging fields:
  Refrigeration, Remediation of gaseous emissions, Fuel (energy density of 11.5 MJ/L), …

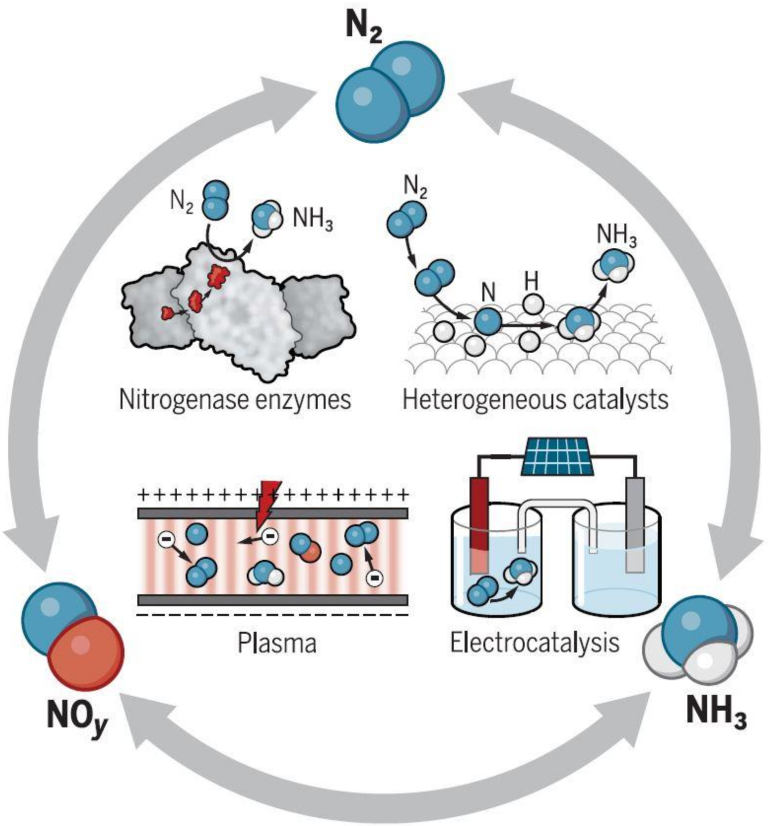


Nature Geoscience 2008, 1: 636-639

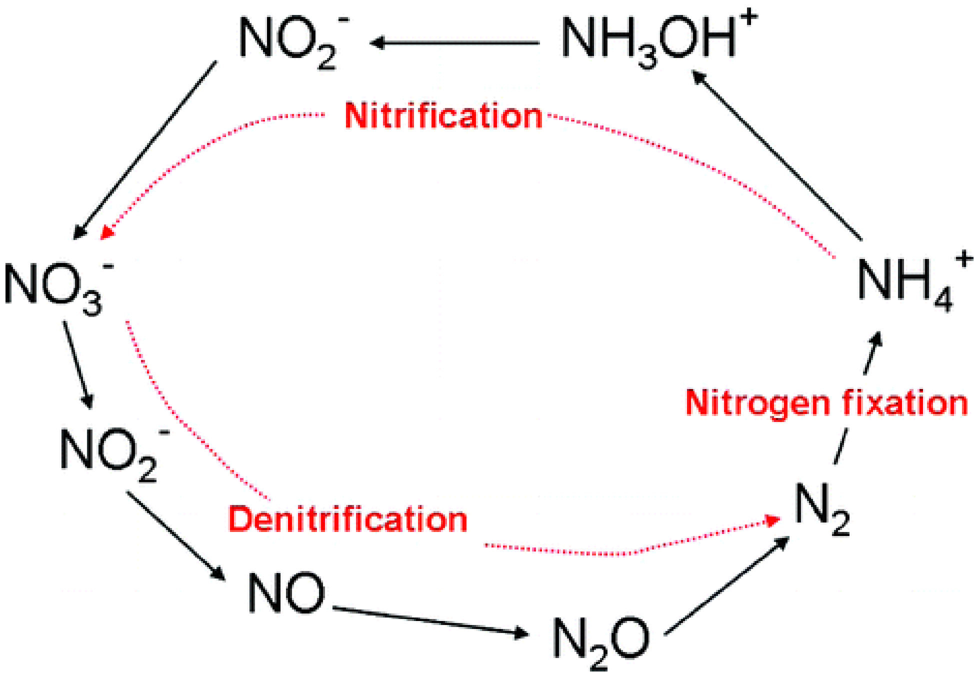


AmVeh by Korea Institute for Energy Research (2013)

Nitrogen Cycle



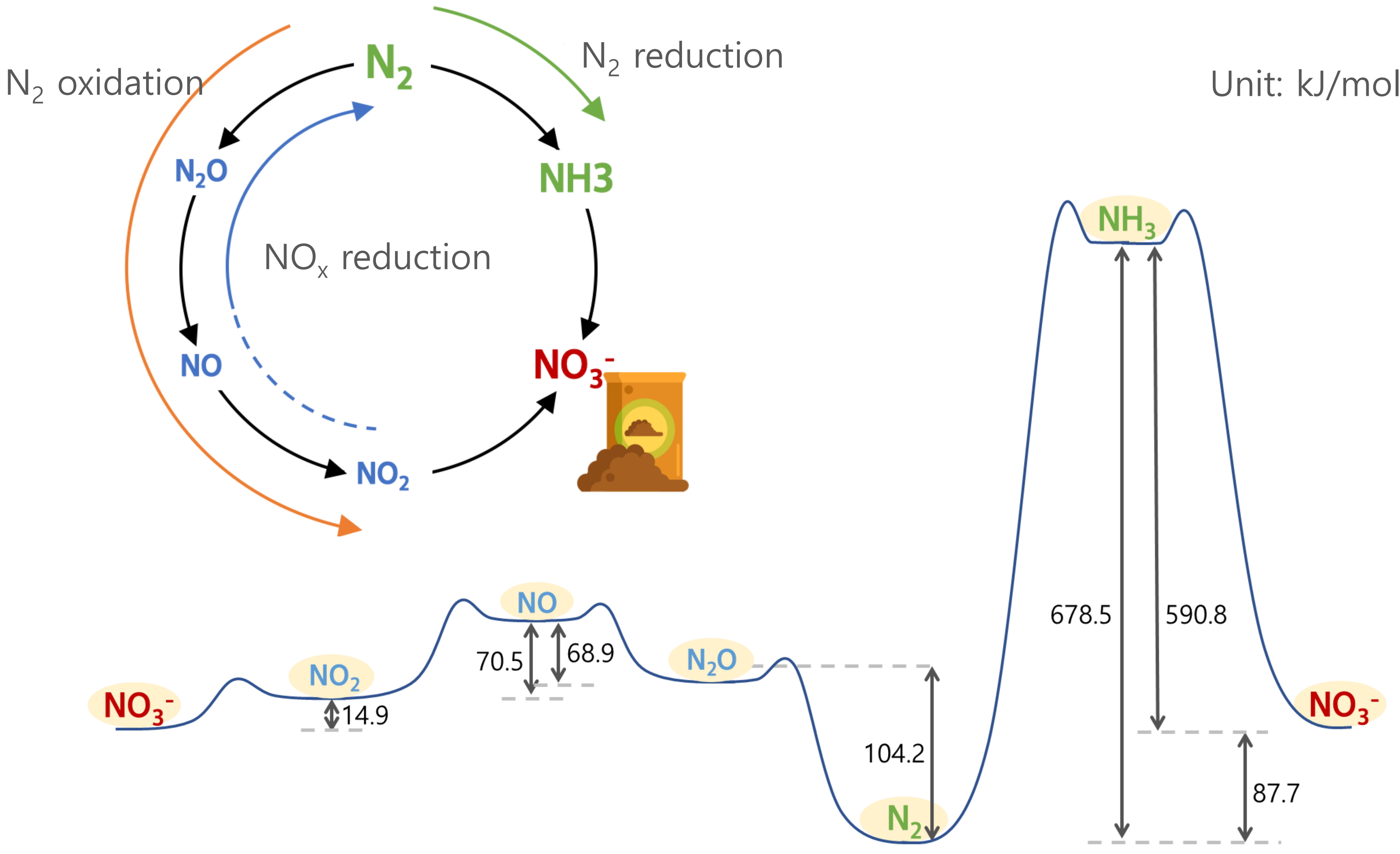
Chen et al., Science 360, 873 (2018)



Chem. Rev., 2009, *109*

Nitrogen fixation is the process by which gaseous nitrogen (N_2) is converted to ammonia (NH_3 or NH_4^+) via biological fixation or nitrate (NO^{3-}) through high-energy physical processes. N_2 is extremely stable and a great deal of energy is required to break the bonds that join the two N atoms

Nitrogen Cycle



Industrial Production of Ammonia

- **Haber-Bosch Process (1909)**
  $N_2 + 3H_2 \rightarrow 2NH_3$ (ΔH^o = -45.8 kJ mol^{-1})
  (150-250 bar, 400-500 °C)

- **Catalysts for Haber-Bosch process**
  -Osmium (1st by Haber), Uranium (2nd by Bosch)
  -BASF: Iron promoted with K_2O, CaO, SiO_2, and Al_2O_3

- **Reaction mechanism**
  1.N_2 (g) → N_2 (adsorbed)
  2.N_2 (adsorbed) → 2 N (adsorbed) (RDS)
  3.H_2 (g) → H_2 (adsorbed)
  4.H_2 (adsorbed) → 2 H (adsorbed)
  5.N (adsorbed) + 3 H(adsorbed)→ NH_3 (adsorbed) (NH → NH_2 → NH_3)
  6.NH_3 (adsorbed) → NH_3 (g)

- **3-5% of the world's natural gas production is consumed in the H-B process. (around 1–2% of the world's annual energy supply)**

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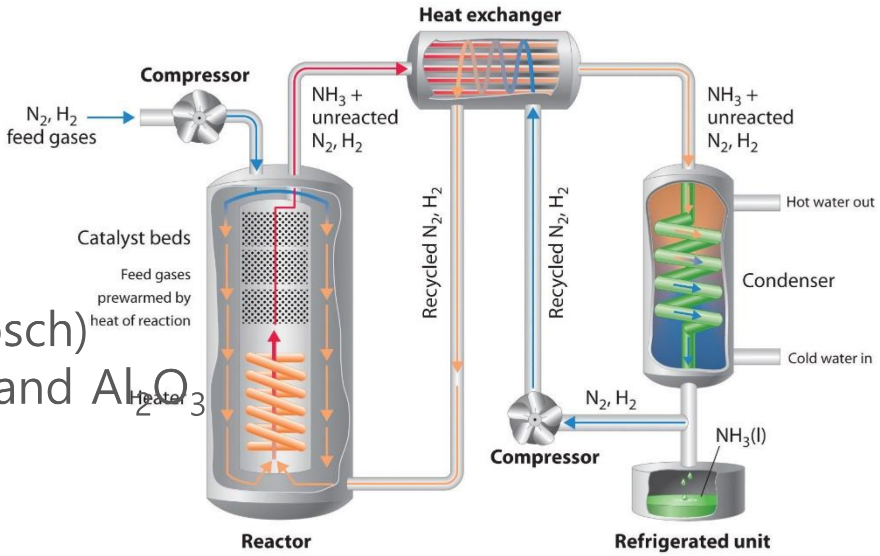

https://www.sciencemag.org/news/2018/07/ammonia-renewable-fuel-made-sun-air-and-water-could-power-globe-without-carbon

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  1. N_2 (g) → N_2 (adsorbed)
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  3. H_2 (g) → H_2 (adsorbed)
  4. H_2 (adsorbed) → 2 H (adsorbed)
  5. N (adsorbed) + 3 H(adsorbed)→ NH_3 (adsorbed) ($NH \rightarrow NH_2 \rightarrow NH_3$)
  6. NH_3 (adsorbed) → NH_3 (g)

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Ammonia

Demand of Ammonia

✓ Nitrogenous Fertilizers : **$ 19.5B**
✓ Ammonia : **$ 5.16B**
✓ Ammonium nitrate, including solution **$: 1.96B**
✓ Ammonium sulphate : **$ 1.98B**
✓ Ammonium nitrate limestone etc mixes
(Calcium **ammonium nitrate** or CAN,) : **$ 1.82B**
✓ Urea-ammonium nitrate mixes in solution : **$ 1.33B**
→ Total : 31.75 B$


<Nitrogenous Fertilizers>


<Ammonia>


<Ammonium Nitrate solution>


<Ammonium sulphate>


<Ammonium Nitrate limestone>


< Urea-ammonium Nitrate mixes in solution>

Global Trends

✓ **Campfire alliance project**

- **Goal**

1. Convert and store wind energy into ammonia fuel
2. Develop, manufacture and export technology for the application of ammonia fuel to ships.

- **Participating institution**

1. Provincial cities supported by Germany (Rostock, Greifswald, Stralsund, Ukermark)

https://wir-campfire.de/

✓ **Alkammonia project**

- **Goal**

1. Convert ammonia to power for hydrogen fuel car

- **Participating institution**

1. AFC Energy (UK) supported by European union

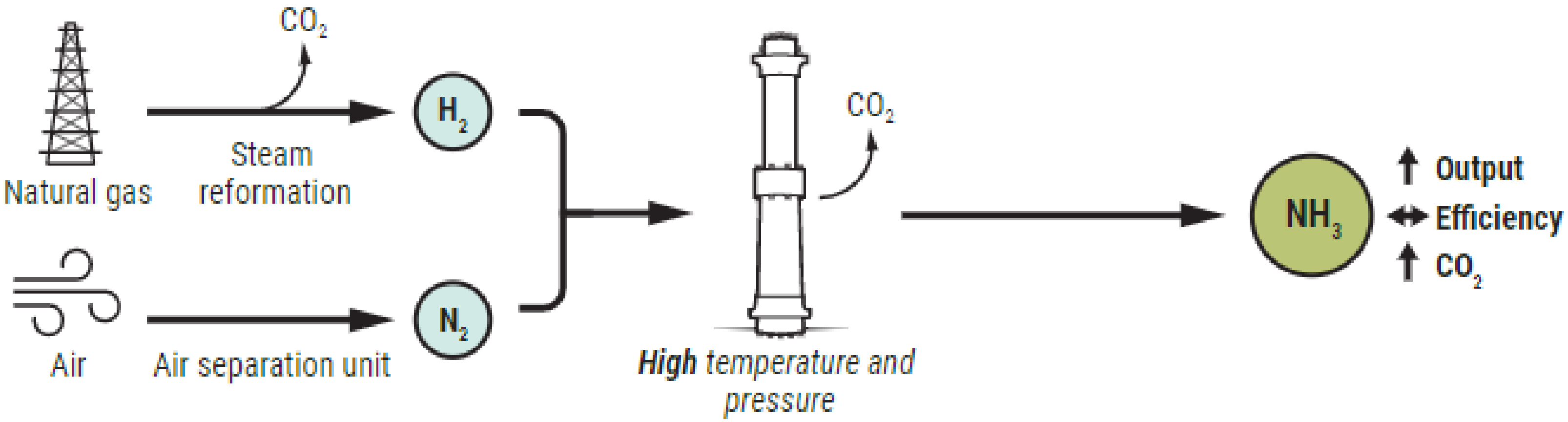
- **Application**

1. Off-grid electric solution
2. Electric car charge system

http://alkammonia.eu/

Ammonia Synthesis in Industry

Ammonia Synthesis in Industry



- **N_2 + $3H_2$ → $2NH_3$** **(ΔH^o = -45.8 kJ mol^{-1})**
  (~ 150 bar, ~ 400 °C at Haber-Bosch)
- NH_3 is **produced 180 million ton** through Haber-Bosch process. (2016)
- About **1-2%** of the world's annual energy supply is consumed by NH_3 power plants. **(34.4 GJ/ton NH_3)**
- Synthesis efficiency about **70%** at industrial scale.
- Large scale facilities and total **energy loss** is **6.49 GJ/t NH_3**
  (Steam reformation loss 4.94 GJ/t NH_3, NH_3 synthesis loss 1.55 GJ/t NH_3)
- The emission of CO_2 is **3.45 $kg/kg_{[NH3]}$**

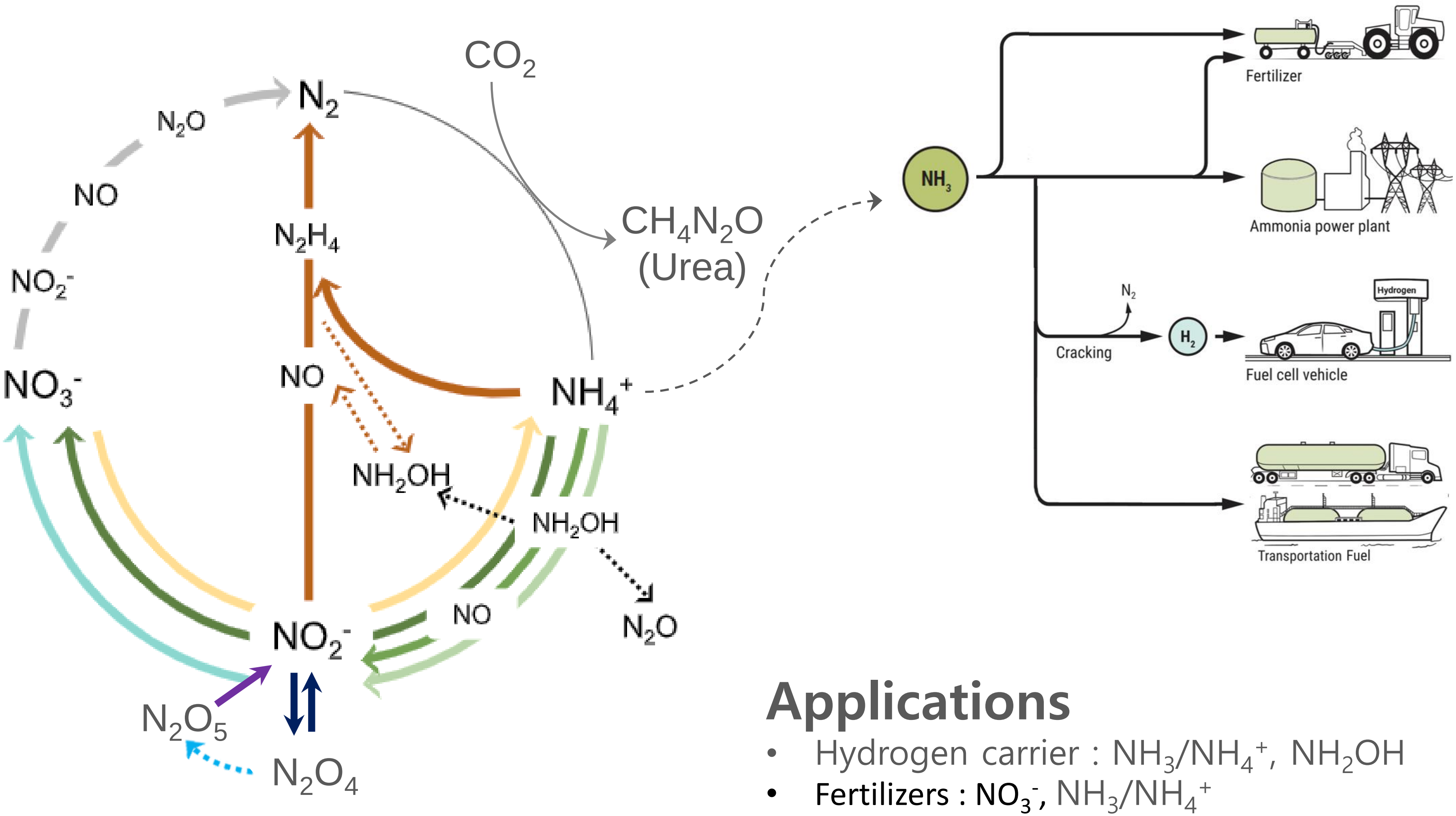
Strength and Weakness of Ammonia Fuels

	MGO*	LNG**	Bio gas	**Bio diesel**	Methanol	**Ammonia**	Hydrogen
Fuel Type	Fossil fuel		Carbon-neutral fuel				
Storage Condition	Ambient temperature and pressure	- 162 °C	- 162 °C	Ambient temperature and pressure	Ambient temperature and pressure	- 34 °C or 10 bar	- 253 °C
Relative Fuel Tank Size	1	~ 2.3	2.3	1	2.3	4.1	7.6
Relative CAPEX	1	~ 1.3	~ 1.3	1	~ 1.15	~ 1.2	Very expensive
Fuel cost & Availability	Less expensive and rich reserves		Difficult to mass produce due to the fuel sourcing problem	Difficult to forecast the price due to unstable supply and demand and the food security problem	High cost of CO_2 capture (from air)	Expensive but relatively low priced for carbon-neutral fuel	Reasonable fuel production cost but high storage and transport cost

🟪 Excellent 🟩 Acceptabl🟥 Undesirable

*MGO: 선박용 경유
**LNG: 액화천연가스

Nitrogen Cycle

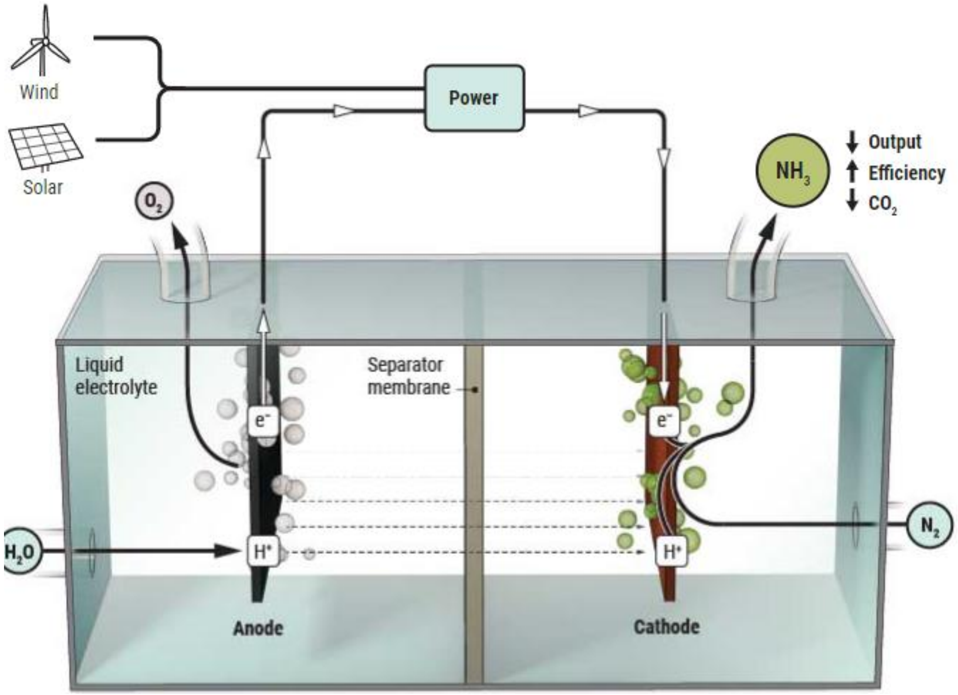


Applications

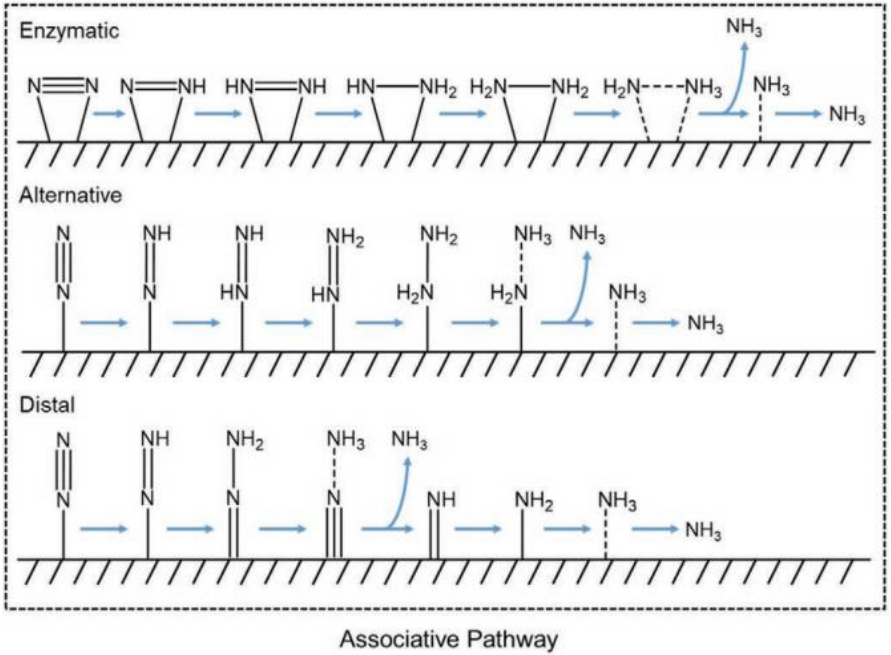
- Hydrogen carrier : NH_3/NH_4^+, NH_2OH
- Fertilizers : NO_3^-, NH_3/NH_4^+
- Fuel : NH_3/NH_4^+, N_2O_4, N_2H_4
- Etc. : N_2O (general anesthesia),CH_4N_2O(urea)

Introduction

Electrochemical NH_3 synthesis



AAAS, DOI:10.1126/science.aau7489



Adv. Energy Mater. 2020, 2000659

- Overall reaction at *pH*=0

$N_2\ (g) + 6H^+ + 6e^- = 2NH_3\ (g)$ $E^O = +0.55$ V *vs.* a reversible

$2H^+ + 2e^- = H_2\ (g)$ $E^O = 0$ V *vs.* RHE R2

$N_2\ (g) + H^+ + e^- = N_2H$ $E^O = -3.2$ V vs. RHE R3

$N_2\ (g) + 2H^+ + 2e^- = N_2H_2\ (g)$ $E^O = -1.10$ V vs. RHE R4

$N_2\ (g) + 4H^+ + 4e^- = N_2H_4\ (g)$ $E^O = -0.36$ V vs. RHE R5

- Overall reaction at *pH*=14

$N_2 + 6H_2O\ (l) + 6e^- = 2NH_3\ (g) + 6OH^-$ $E^O = -0.148$ V *vs.* RHE R6

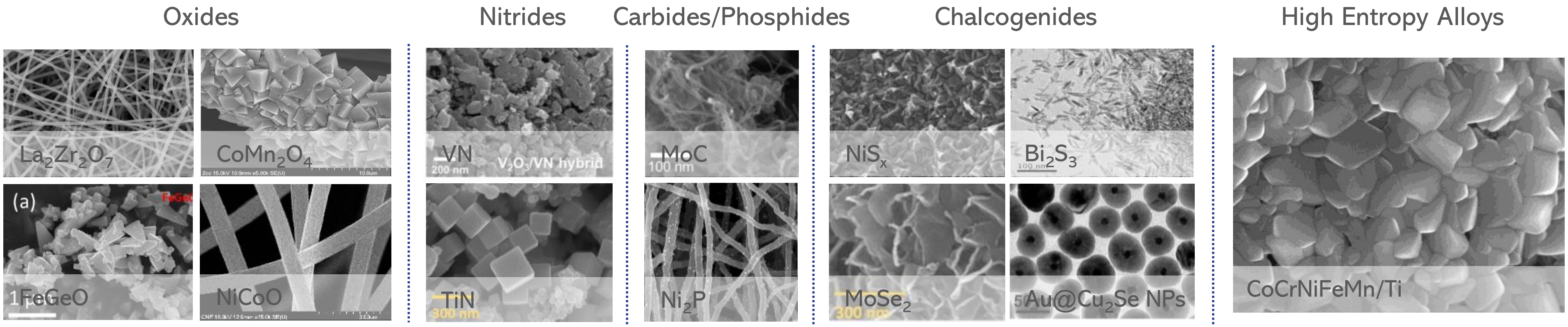
$2H_2O\ (l) + 2e^- = H_2\ (g) + 2OH^-$ $E^O = -0.828$ V *vs.* RHE R7

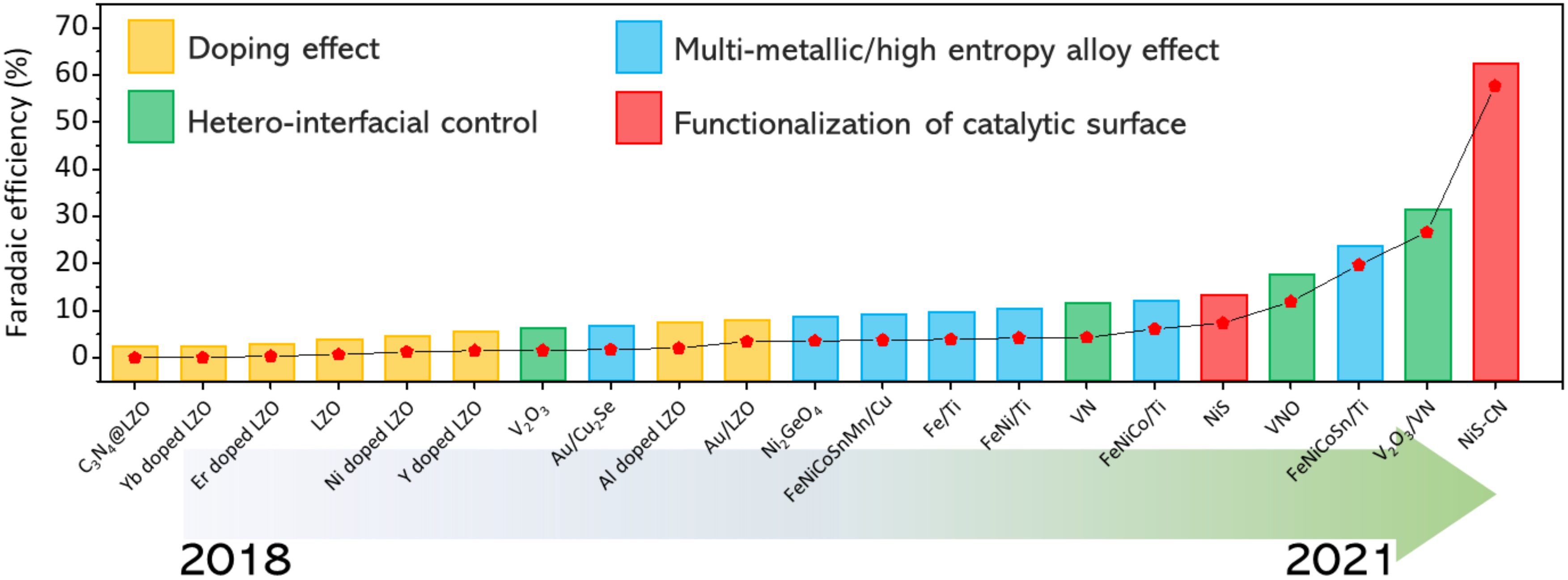
$N_2\ (g) + 4H_2O\ (l) + 6e^- = N_2H_4\ (g) + 4OH^-$ $E^O = -1.16$ V vs. RHE R8

$N_2\ (g) + 4e^- = N_2^-\ (aq)$ $E^O = -3.37$ V vs. RHE R9

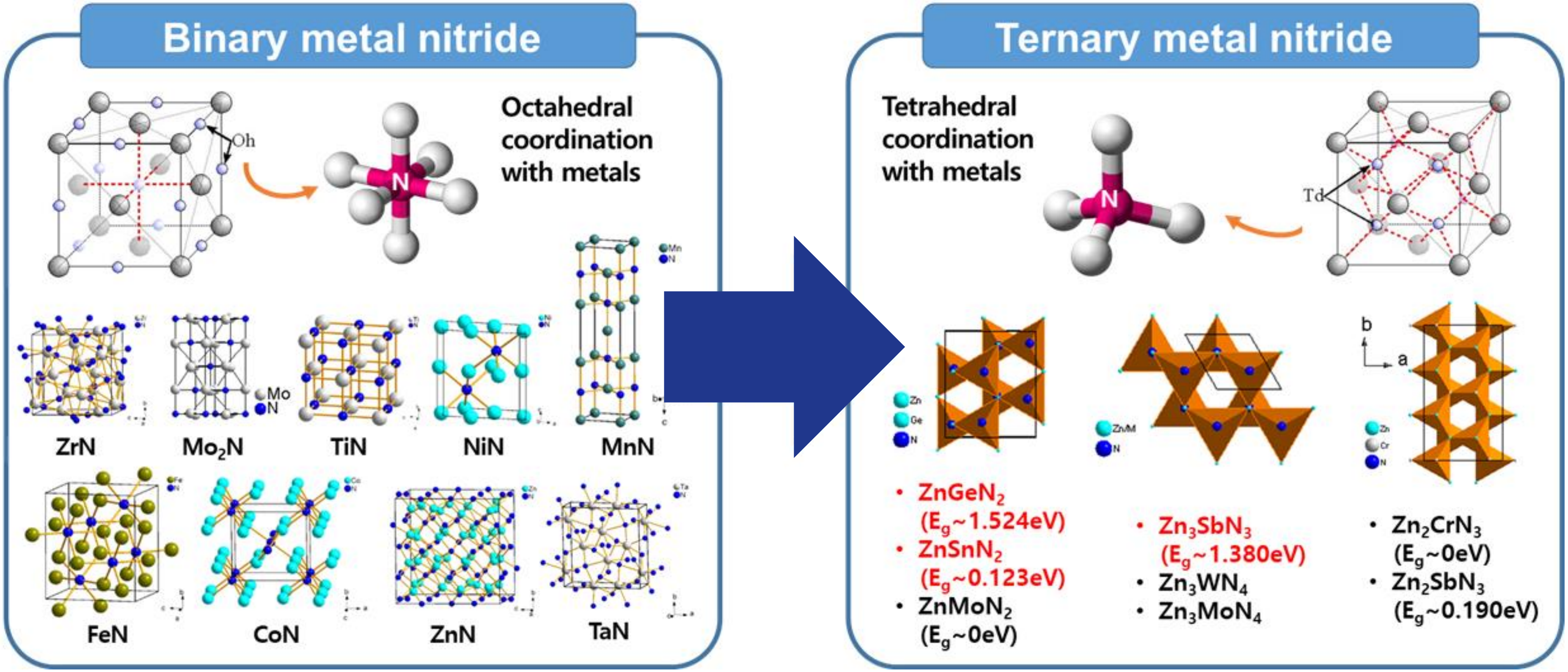
Performance Chart from Our Group

Catalysts for electrochemical N_2 reduction to NH_3 production





Candidate metal nitride-based materials for NRR



Binary metal nitride

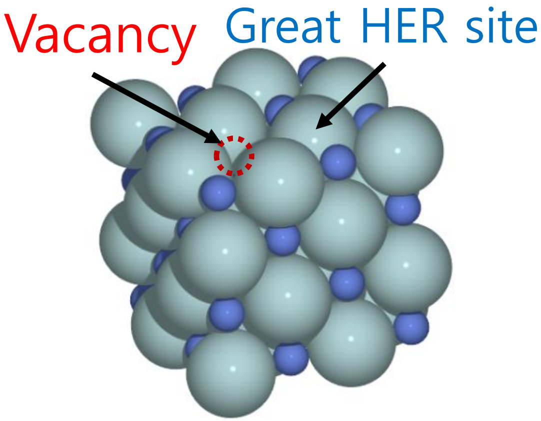
Octahedral coordination with metals

Ternary metal nitride

Tetrahedral coordination with metals

- $ZnGeN_2$ (E_g~1.524eV)
- $ZnSnN_2$ (E_g~0.123eV)
- $ZnMoN_2$ (E_g~0eV)
- Zn_3SbN_3 (E_g~1.380eV)
- Zn_3WN_4
- Zn_3MoN_4
- Zn_2CrN_3 (E_g~0eV)
- Zn_2SbN_3 (E_g~0.190eV)

Zirconium Nitride (ZrN)



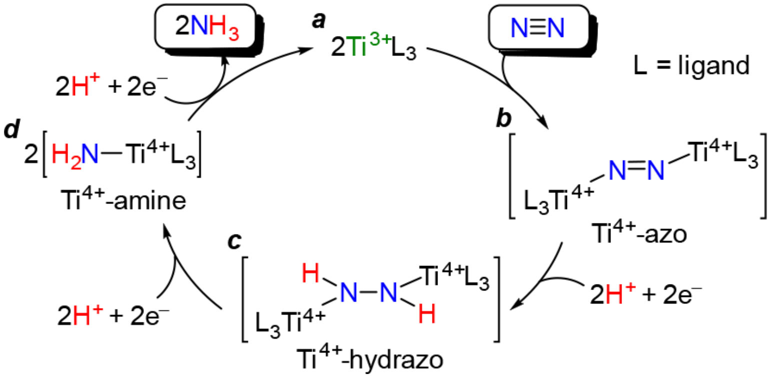
Brian and Aayush from Norskov group

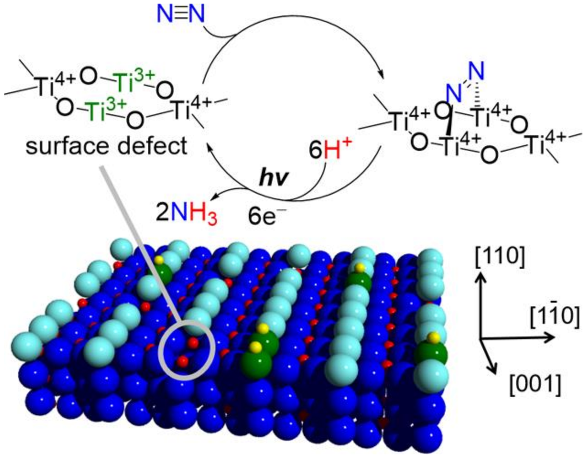
- Find catalyst where N_2^* is more stable than H^* at the limiting potential.
- ZrN vacancies have this property.
- Top sites are excellent HER catalysts.

- **ZrN**
  - The lowest bulk resistivity (~13.6 μΩ) and high thermal stability among group IV and V transition metal nitrides
  - Investigated as wear resistant coatings, optical coatings, functional multi-layers, high T superconductors, thermoelectrics, etc.
  - Promising materials for ULSI applications such as a diffusion barrier for Cu interconnects and contact metal in III-V semiconductor devices, in high density memory structures.

Ti Characteristic

N2 active site

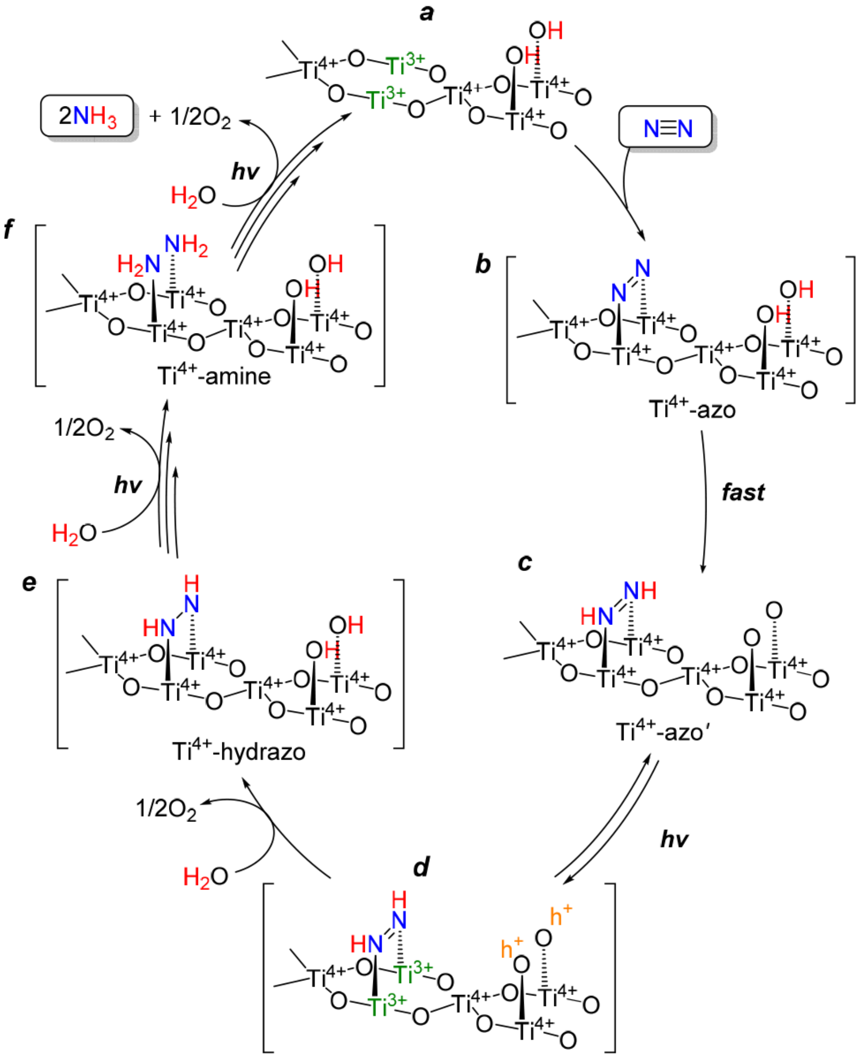




J. Am. Chem. Soc. 2017, 139, 10929–10936

- **For NRR, Creation of active sites that efficiently promote N≡N cleavage is necessary**
- **For photocatalytic conversion, Ti3+ ions on TiO2 can react and bond with N2 gas through electron donation.**

Active Mechanism of Ti3+



J. Am. Chem. Soc. 2017, 139, 10929–10936

- **Ti3+ ions present by surface defects (oxygen vacancies) act as an active site to trap nitrogen gas. (a -> b)**
- The adsorbed N2 interacts with H atoms of the
- adjacent surface Ti−OH and produces Ti4+−azo′ species. (b -> c)
- **Photoexcitation of TiO2 with Ti4+−azo′ species creates CB e− and VB h+ pairs. (c -> d)**
- The N=N dissociation on the Ti3+ produces Ti4+ hydrazo species with the water oxidation by the h+. (d -> e)
- Once more, the H atom in oxygen combines with NH to form NH2. (e -> f -> a)