Theoretical Calculations of Electrochemical Ammonia Synthesis at Ambient Pressure and Temperature

Egill Skúlason\textsuperscript{1,2}, Thomas Bligaard\textsuperscript{1,2}, Jan Rossmeisl\textsuperscript{2}, Áshildur Logadóttir\textsuperscript{2}, Jens K. Nørskov\textsuperscript{2}, Hannes Jónsson\textsuperscript{1}

\textsuperscript{1}Science Institute, University of Iceland, Dunhagi 3, VR-II, 107 Reykjavik, Iceland
\textsuperscript{2}CAMP, NanoDTU, Department of Physics, Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark
Contents

• Ammonia Synthesis (AS)
  – Industrial vs. Biological
  – Why another AS method?
  – Formation of NH₃ in Electrochemical Cell

• Methodology
  – Density Functional Theory (DFT)
  – Free Energy and Electrochemical Model

• Results & Discussions
  – AS in Electrochemical Cell
  – Stability of Intermediates
  – Hydrogen Evolution Reaction (HER)
  – Experiments on Electrochemical AS

• Further Studies & Conclusions
Industrial Ammonia Synthesis

Haber-Bosch Method

*Dissociative Mechanism*

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

40 x 10^6 tonnes/year

430 °C

150 atm.


Biological Ammonia Synthesis

**Associative Mechanism**

\[ \text{N}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow 2\text{NH}_3 + \text{H}_2 \]

16 ATP → 16 ADP + 16 P_i + 5 eV

20 °C

1 atm.


Why another AS method?

• The Haber-Bosch process
  – High pressure and temperature
  – Large-scale chemical plants

• Worldwide regulations for NO$_x$ emission
  – Ammonia expected to be a reductant of NO$_x$ emitted from ships and stationary facilities
  – Ammonia synthesis on a small-scale under mild condition
Can we produce ammonia with a mechanism similar to that of Nitrogen fixing enzymes?
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Density Functional Theory (DFT)

• **DFT**
  – *ab initio* method
  – Solves the Schrödinger equation
  – Hohenberg-Kohn theorem (1964)
  – Total energy of a quantum mechanical electron gas is a unique functional of its density $r(r)$
  – Code: *Dacapo* from CAMP

• **Valence electrons**
  – Expanded in plane wave basis set
  – Includes periodic boundary conditions

• **Vanderbilt pseudopotential**
  – The nucleus
  – The core electrons
Free Energy Calculations

DFT energy values converted into free energy values:

\[ \Delta G = \Delta E_{\text{DFT}} + \Delta (ZPE) - T \Delta S \]

ZPE and S: from vibrational frequency calculations in DFT or taken from handbooks of gas phase molecules.

The energy levels of a harmonic oscillator:

\[ E_\nu = (\nu + 1/2)\hbar \omega \quad \omega = (k/m)^{1/2} \quad \nu = 0, 1, 2, \ldots \]

⇒ ZPE: \[ E_0 = 1/2\hbar \omega \]

\[ S = Nk\{\frac{\beta \varepsilon}{(e^{\beta \varepsilon} - 1)} - \ln(1-e^{-\beta \varepsilon})\} \quad \beta \varepsilon = \frac{hc\nu}{kT} \]
Electrochemical Model

- Calculate the free energy at zero potential, $\Delta G(0)$.
- Then the number ($n$) of electrons (with the elementary charge $-e$), multiplied with the cell potential ($U$), is added to $\Delta G(0)$:

$$\Delta G(U) = \Delta G(0) + nU$$

- All states involving an electron will simply be shifted in free energy by $nU$ due to the external potential.

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**Possible Formation of NH₃ in Electrochemical Cell**

*First Step: N₂ Adsorbs on Surface Electrode*

\[ \text{Cathode: } N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \]

\[ \text{Anode: } H_2 \leftrightarrow 2H^+ + 2e^- \]
Possible Formation of NH₃ in Electrochemical Cell

Second Step: A Proton is Transferred from the Electrolyte and an Electron from the Cathode to N₂

Cathode

N₂ + 6H⁺ + 6e⁻ → 2NH₃

Anode

H₂ ↔ 2H⁺ + 2e⁻
Possible Formation of NH₃ in Electrochemical Cell

Last Step: After Adding 6H⁺ and 6e⁻ to N₂, 2NH₃ is formed

\[ \text{Anode} \]
\[ \text{Cathode} \]
\[ N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \]

\[ \text{H}_2 \leftrightarrow 2H^+ + 2e^- \]
Ammonia Synthesis

Free Energy Diagram at 300 K

ΔG = ΔE_{DFT} + Δ(ZPE) - TΔS

Associative Mechanism

Ru(0001) surface
AS in Electrochemical Cell

Free Energy at 300 K and -1.07 V vs. SHE

\[ \Delta G = \Delta E_{\text{DFT}} + \Delta(ZPE) - T\Delta S \]

Anode: \( \text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^- \)

Cathode: \( \text{N}_2 + 6\text{H}^+ + 6\text{e}^- \leftrightarrow 2\text{NH}_3 \)

Over all: \( \text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3 \)

\[ \Delta G(U) = \Delta G(0) + eU \]

\( \text{pH} = 0 \)

Ru(0001) surface
Stability of Intermediates

Ru(0001) surface
T = 300 K, pH = 0

\[ \Delta G(U) = \Delta G(0) + eU \]
The Electrochemical System

Cathode: \[ N_2 + 6H^+ + 6e^- \leftrightarrow 2NH_3 \]

Anode: \[ H_2 \leftrightarrow 2H^+ + 2e^- \]
Hydrogen Coverage on the Electrode Surface

Cathode: $\text{N}_2 + 8\text{H}^+ + 8\text{e}^- \leftrightarrow 2\text{NH}_3 + \text{H}_2$

Anode: $\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$
Hydrogen Evolution on the Electrode Surface

Cathode

\[ \text{N}_2 + 8\text{H}^+ + 8\text{e}^- \leftrightarrow 2\text{NH}_3 + \text{H}_2 \]

Anode

\[ \text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^- \]
Hydrogen Evolution on the Electrode Surface

Cathode

\[ \text{N}_2 + 8\text{H}^+ + 8\text{e}^- \leftrightarrow 2\text{NH}_3 + \text{H}_2 \]

Anode

\[ \text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^- \]
Experiments on Electrochemical AS

\[ \frac{3}{2} \text{H}_2 + \text{N}^3- \rightarrow \text{NH}_3 + 3\text{e}^- \quad \text{1/2 \ N}_2 + 3\text{e}^- \rightarrow \text{N}^3- \]

Over all: \[ \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightarrow \text{NH}_3 \]

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

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• Further Studies & Conclusions
Further Studies

- Finish calculation of the electrochemical ammonia synthesis on a step of the Ru(0001) surface.
- Understand the hydrogen evolution process and find some ways to stop it in the electrochemical ammonia synthesis.
Further Studies

- Apply external electric potential in the calculations
Further Studies

- Apply external electric potential in the calculations
- Calculate the stability of the intermediates
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Electron Density Changes due to External Electric Potential Calculated with DFT
Conclusions

• Our electronic structure calculations predict that it could be possible to electrochemically produce ammonia under ambient reaction conditions.
• Apply a negative voltage on the order of 1.07 V to an electrochemical cell.
• The HER is needed to be suppressed.