Developments in high rate, high selectivity, Li-mediated nitrogen reduction to ammonia

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**Electrochemical Ammonia Production (ambient T,P)**

**Non - Haber-Bosch Process Flow Diagram**

- **Power supply**
- **Water** → **Electrolyser** → **N₂** → **NH₃ Separation Unit** → **NH₃ (Ammonia)**
- **Air** → **Air Separation Unit (ASU)**
The Challenge:

**Nitrogen Reduction reaction (NRR):**

\[ \text{N}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 2\text{NH}_3 \ (g) \quad E^\circ = +0.056 \text{ V vs. NHE} \]

**Competing Hydrogen Evolution Reaction (HER):**

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad E^\circ = 0 \text{ V vs. RHE} \]

Can we suppress the Hydrogen Evolution Reaction to achieve high selectivity towards \text{N}_2 to ammonia?

Suryanto et al Nature Catalysis 2019
MacFarlane et al Adv Materials 2019
Potential Direct Electrochemical Ammonia Production Modalities

“A Roadmap to the Ammonia Economy” Joule (2020)
Li – Mediated Ammonia Synthesis

Constant Current Mode

*J. Electroanal. Chem* (1994)
Selectivity: 42–60% (50 bar)

*ChemElectroChem* (2020)
Selectivity: ca. 10% (ambient P)

Selectivity: ca. 19–35% (ambient P)

Cell voltage: up to 20 V

**State of the Art:**
(constant current mode)

Salt (Mediator): \( \text{Li(CF}_3\text{SO}_3) \)
Solvent: Tetrahydrofuran, THF
Proton Source: Ethanol

**Water**
**Li – Mediated Ammonia Synthesis**

**OPTIMISATION PARAMETERS**

- Faradaic Efficiency, % (=selectivity)
- NH₃ formation rate, g m⁻² s⁻¹

**Graphs:**
- Faradaic Efficiency, % (=selectivity)
- NH₃ formation rate, g m⁻² s⁻¹

**Experiment run #**
Since the first report on Li-mediated NRR in 1993, the electrochemical cell has not evolved very much....

- THF is still the typical solvent of choice
- EtOH is still used as a proton source
- Cu as the cathode material
- Pt as the anode material
Electrolyte Engineering

Electrolyte development is the key!

Electrolyte Requirements:

- High ionic conductivity
- Low water solubility (hydrophobic)
- Chemically stable
- Non-sacrificial
Li-eNRR in the MU-2020 Engineered Electrolyte

Performance overview

**Highly conductive electrolyte**

- 30x more conductive than conventional electrolyte

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*N₂ pressure dependence*

- Average cell voltage (V): 4.0 - 4.8 V
- Maximum NH₃ selectivity (Faradaic efficiency %): 84% ± 11%
- Maximum NH₃ production rate: 48 ± 12 g m⁻² h⁻¹
**Electrochemical stability comparison to the conventional electrolyte**

**Conventional electrolyte**
(0.2 M LiBF₄ + 0.17 M EtOH in THF)

- **Current density**: 8 mA cm⁻²
- **Cell lifetime**: 18 minutes
- **Cell voltage**: > 12 V
- **NH₃ Yield rate**: 8.6 g m⁻² h⁻¹
- **NH₃ Selectivity**: 47.4%

**MU-2020**

- **Current density**: 22.5 mA cm⁻²
- **Test duration**: > 1200 minutes
- **Cell voltage**: < 5 V
- **NH₃ Yield rate**: 43.5 g m⁻² h⁻¹
- **NH₃ Selectivity**: 92%
- **Energy efficiency**: 25%
**ARENA milestones, literature target & performance projection**

- **Our work** – highest recorded: 120 g m\(^{-2}\) h\(^{-1}\)
- **Literature** – Max EE = 2.8%
  - 1994\(^3\)
  - 2019\(^4\)
  - 2020\(^5\)
- **Target – DoE REFUEL**\(^2\)
- **Target – Giddey et al (CSIRO)**\(^1\)

**NH\(_3\)** production rate (g m\(^{-2}\) h\(^{-1}\))

- **Literature target (Giddey et al)**
  - 60 g m\(^{-2}\) h\(^{-1}\)
- **ARENA Monash ARENA Project target**

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\(^1\) Int. J. Hydrogen Energy, 38, p.14576

\(^2\)ARPA-E (2016). REFUEL.

\(^3\)J. Electroanal. Chem. (1994), 367, p. 183

\(^4\)Joule (2019), 3, p. 1127

\(^5\)Nature Catalysis (2020), 3, p. 463
Our strategy to reach the DoE’ target for production rate

- Development of high specific surface area electrodes
  - Metal foam
  - 3D printed metal electrodes

Scale-up strategy to further increase production rate

Prototyping a 1 kW flow cell
Acknowledgement

The Hydrogen/Ammonia Team