ARC Centre of Excellence for Electromaterials Science

MONASH University

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

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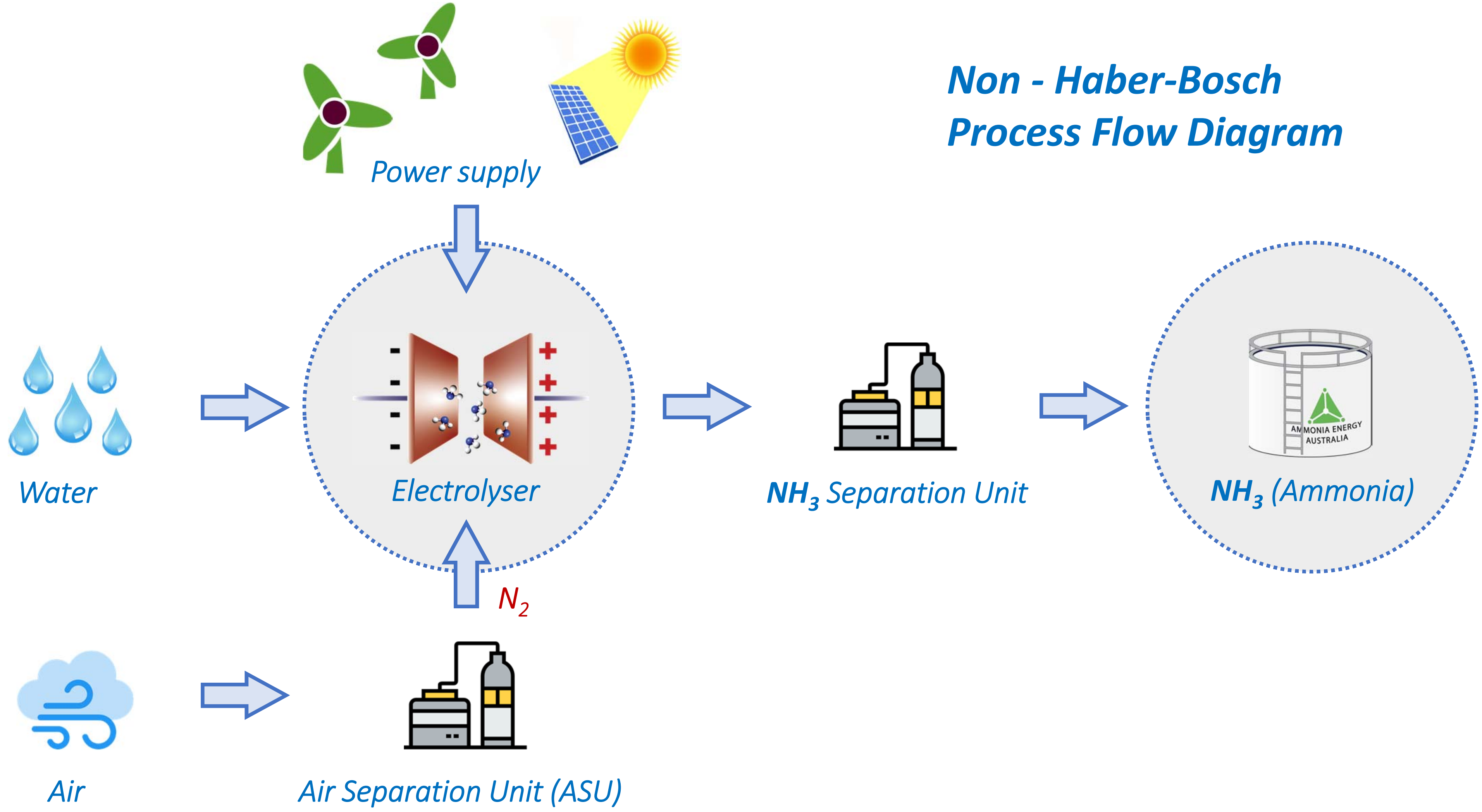
Monash University

Australian Government
Australian Research Council

Australian Government
Australian Renewable Energy Agency

ARENA

Electrochemical Ammonia Production (ambient T,P)

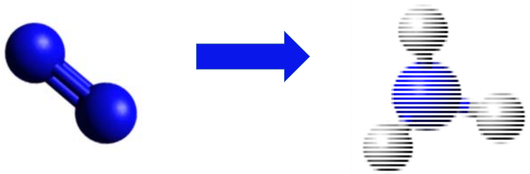


Electrochemical Ammonia Synthesis

The Challenge:

Nitrogen Reduction reaction (NRR):

$N_2 + 6H^+ + 6e^- \rightarrow 2NH_{3\ (g)}$ $E^\circ = +0.056$ V vs. NHE



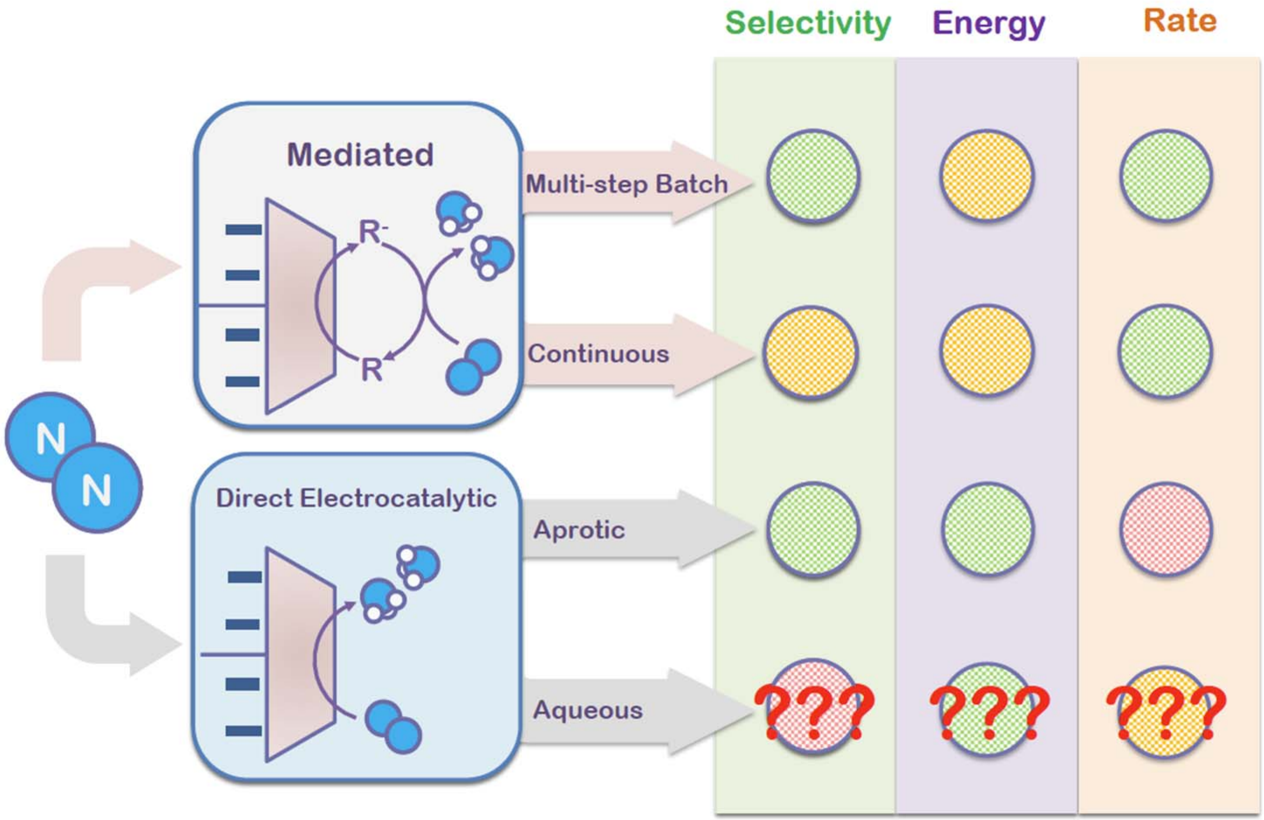
Competing Hydrogen Evolution Reaction (HER):

$2H^+ + 2e^- \rightarrow H_2$ $E^\circ = 0$ V vs. RHE

Can we suppress the Hydrogen Evolution Reaction to achieve high selectivity towards N_2 to ammonia?

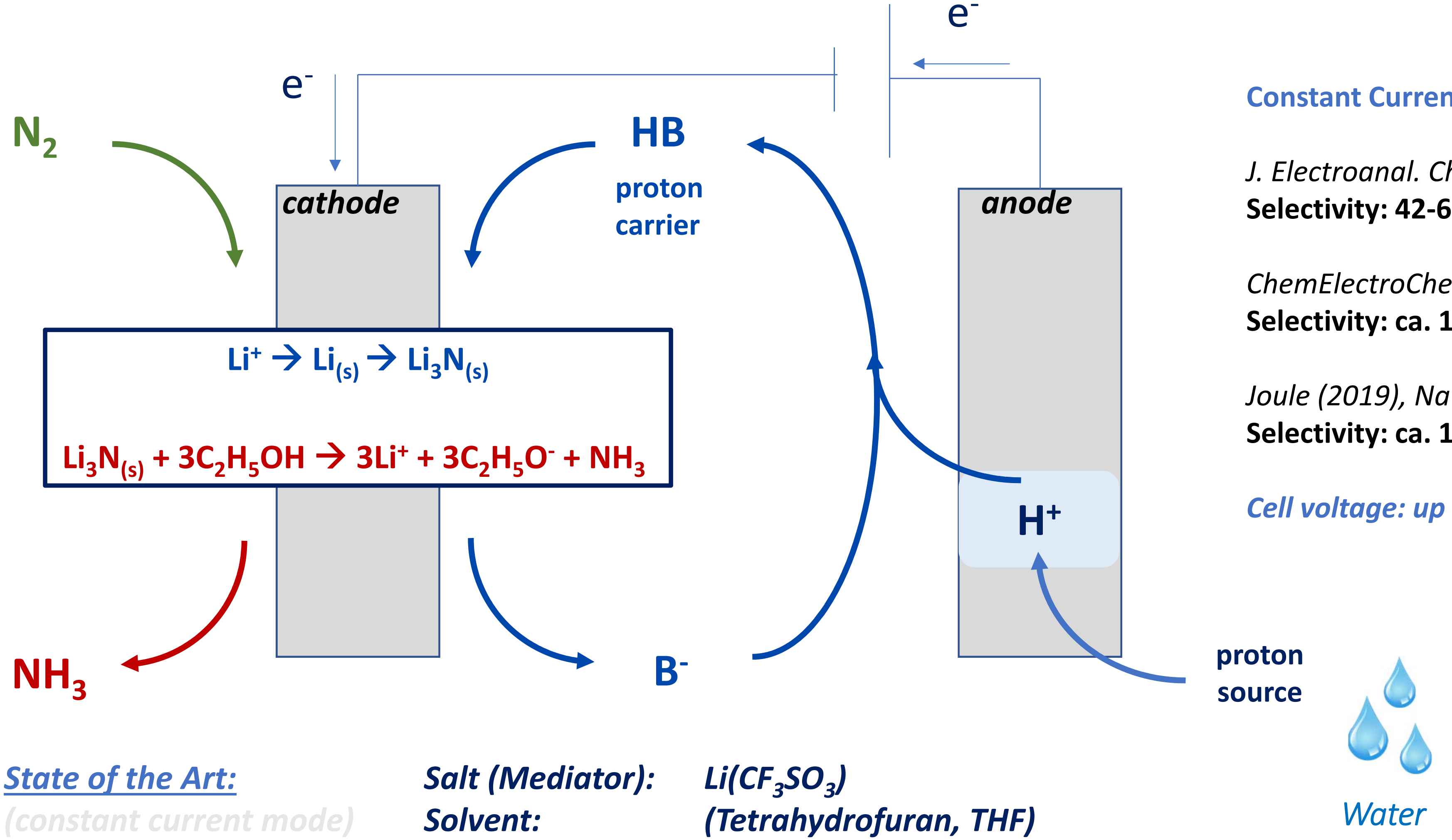
Suryanto et al Nature Catalysis 2019
MacFarlane et al Adv Materials 2019

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)*

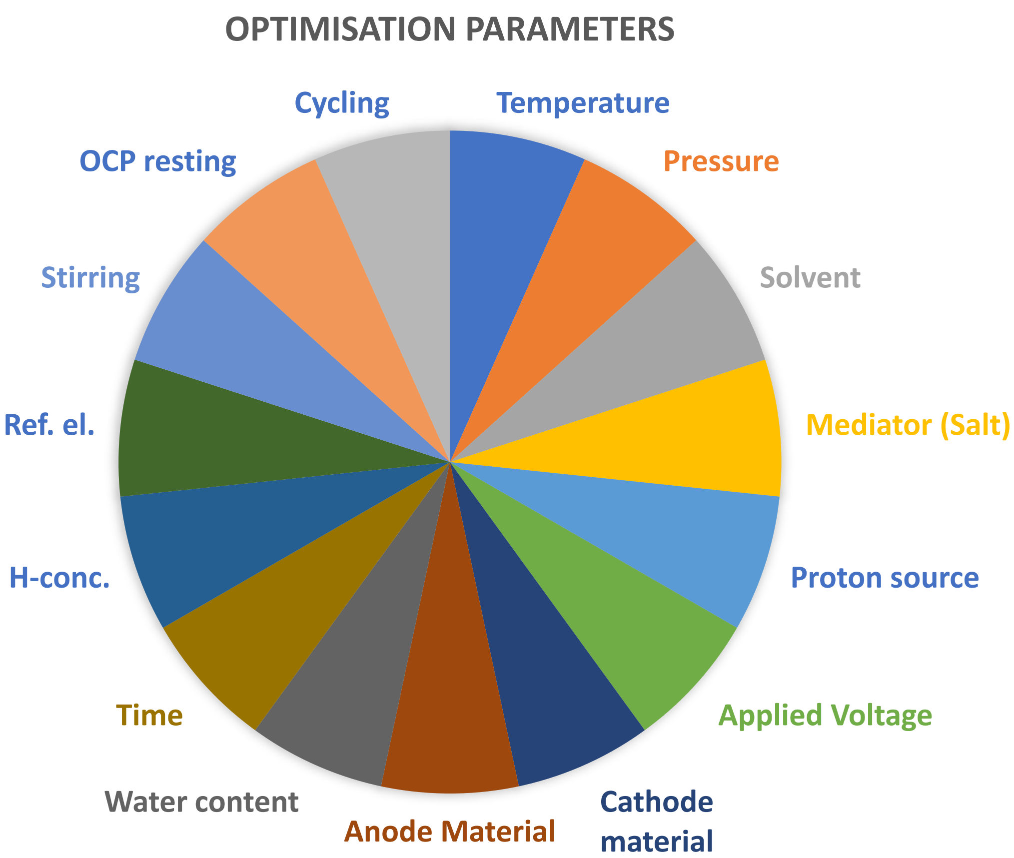
Joule (2019), Nat. Catal. (2020)
Selectivity: ca. 19-35% *(ambient P)*

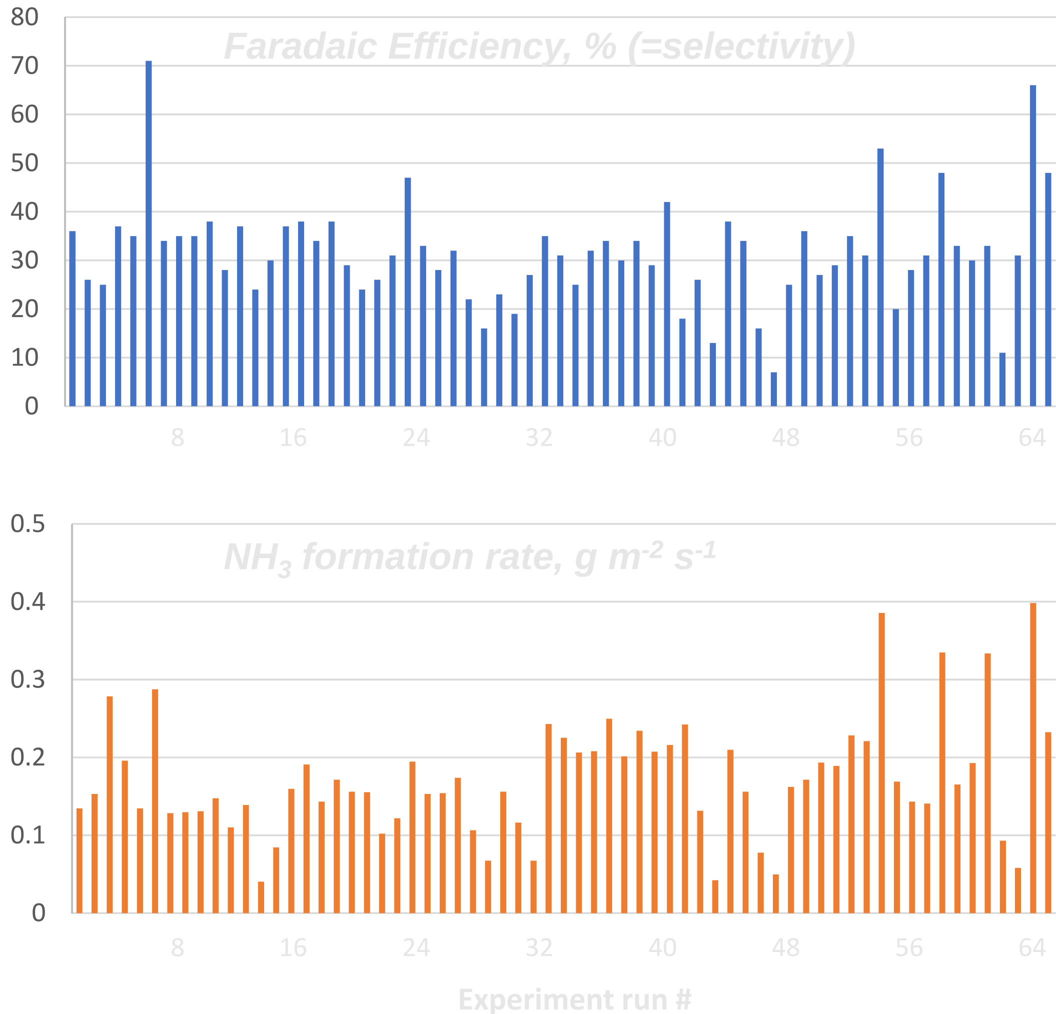
Cell voltage: up to 20 V

State of the Art:
(constant current mode)

Salt (Mediator):	***$Li(CF_3SO_3)$***
Solvent:	***(Tetrahydrofuran, THF)***
Proton Source:	***Ethanol***

Li – Mediated Ammonia Synthesis

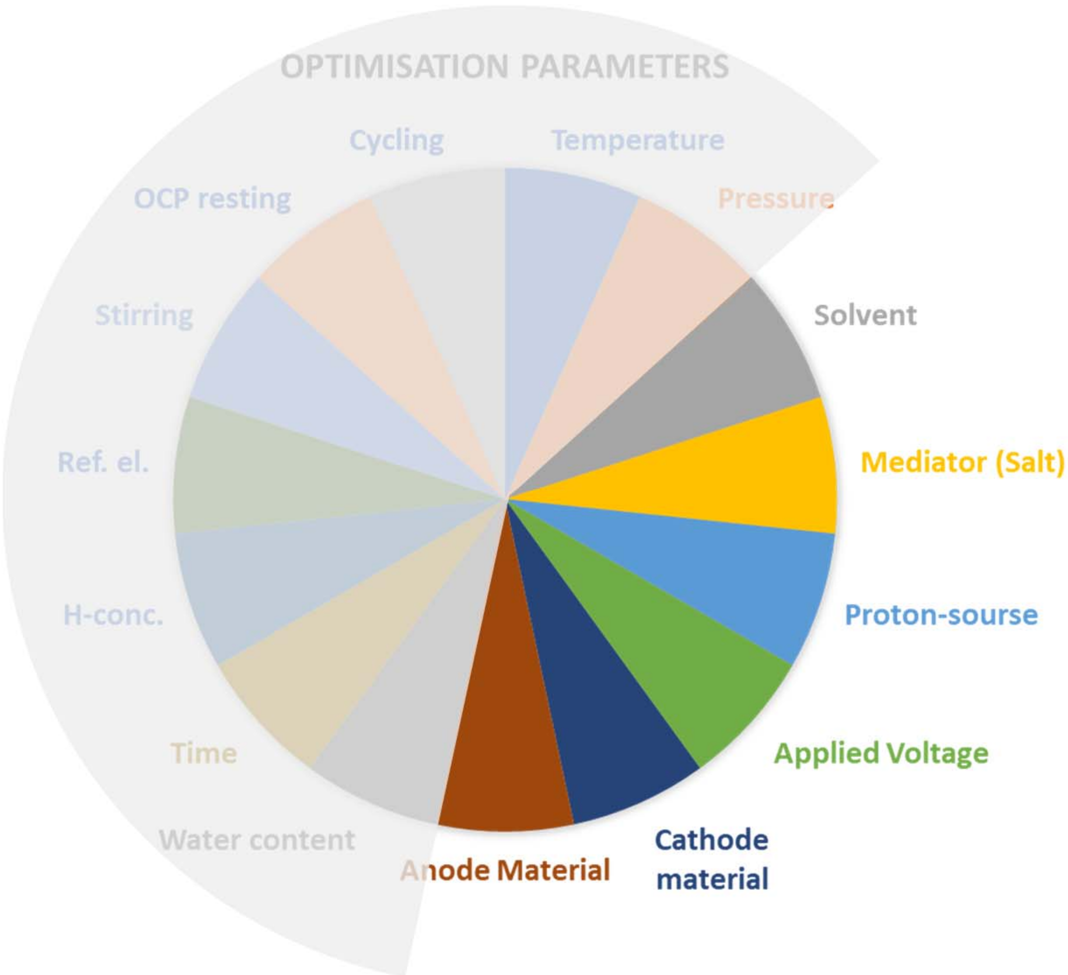




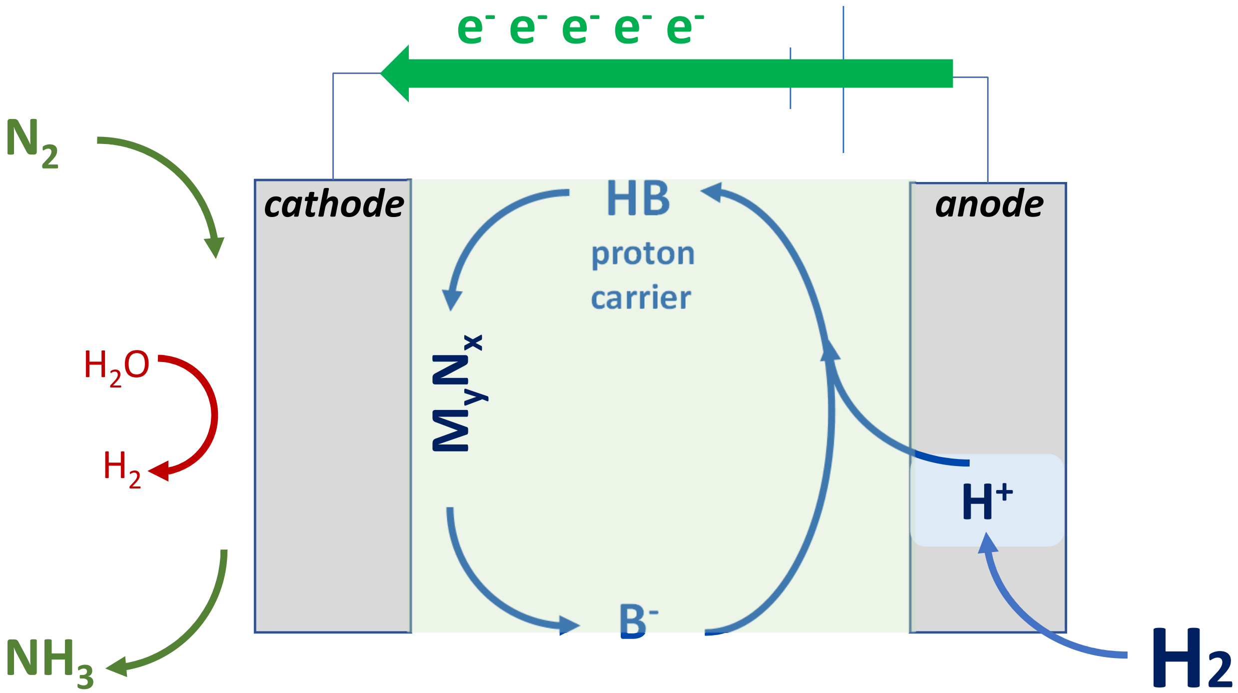
Identifying the inherent issues

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



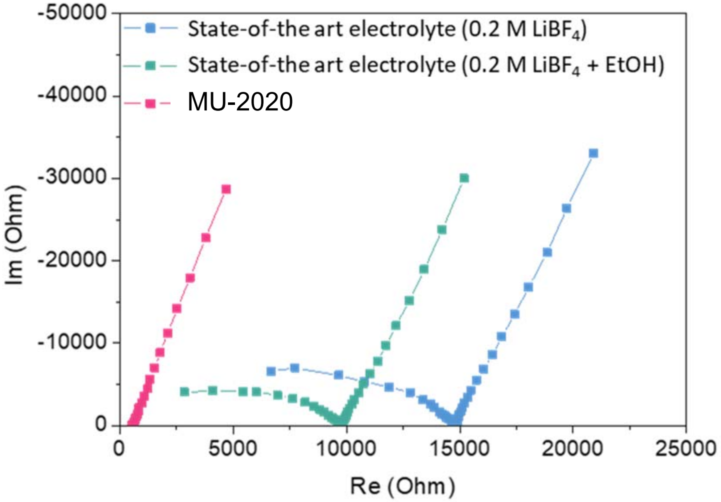
Electrolyte development is the key!

Electrolyte Requirements:

- **High ionic conductivity**
- **Low water solubility (hydrophobic)**
- **Chemically stable**
- **Non-sacrificial**

Li-eNRR in the MU-2020 Engineered Electrolyte

Highly conductive electrolyte



30x more conductive than conventional electrolyte

Performance overview

Average cell voltage (V)	**4.0 - 4.8 V**
Maximum NH_3 selectivity (Faradaic efficiency %)	**84% ± 11%**
Maximum NH_3 production rate	**48 ± 12** *$g\ m^{-2}\ h^{-1}$*

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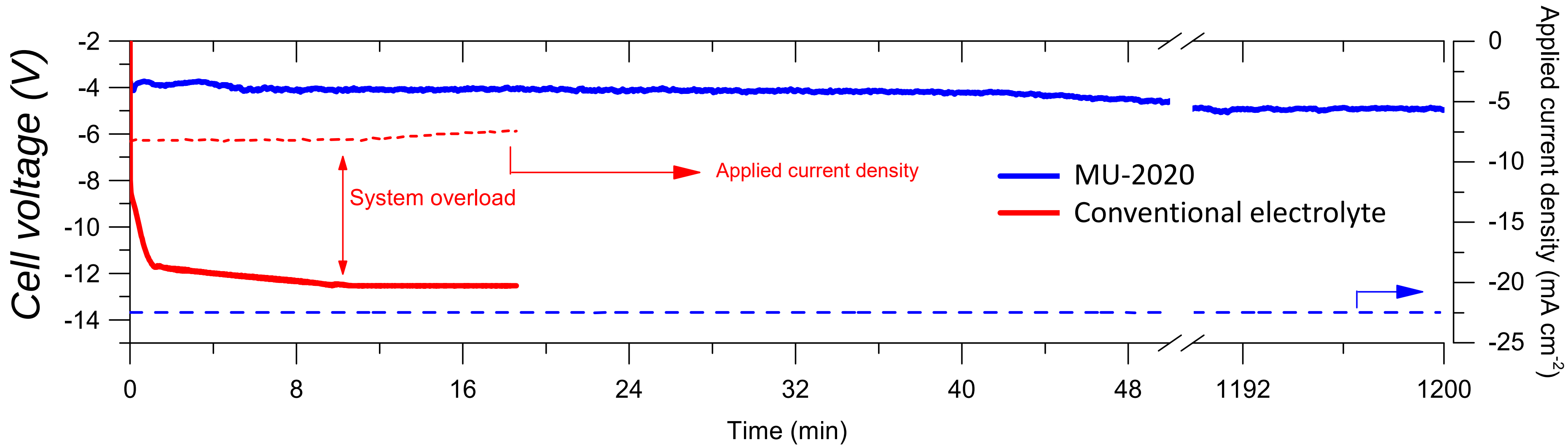
Electrochemical stability comparison to the conventional electrolyte



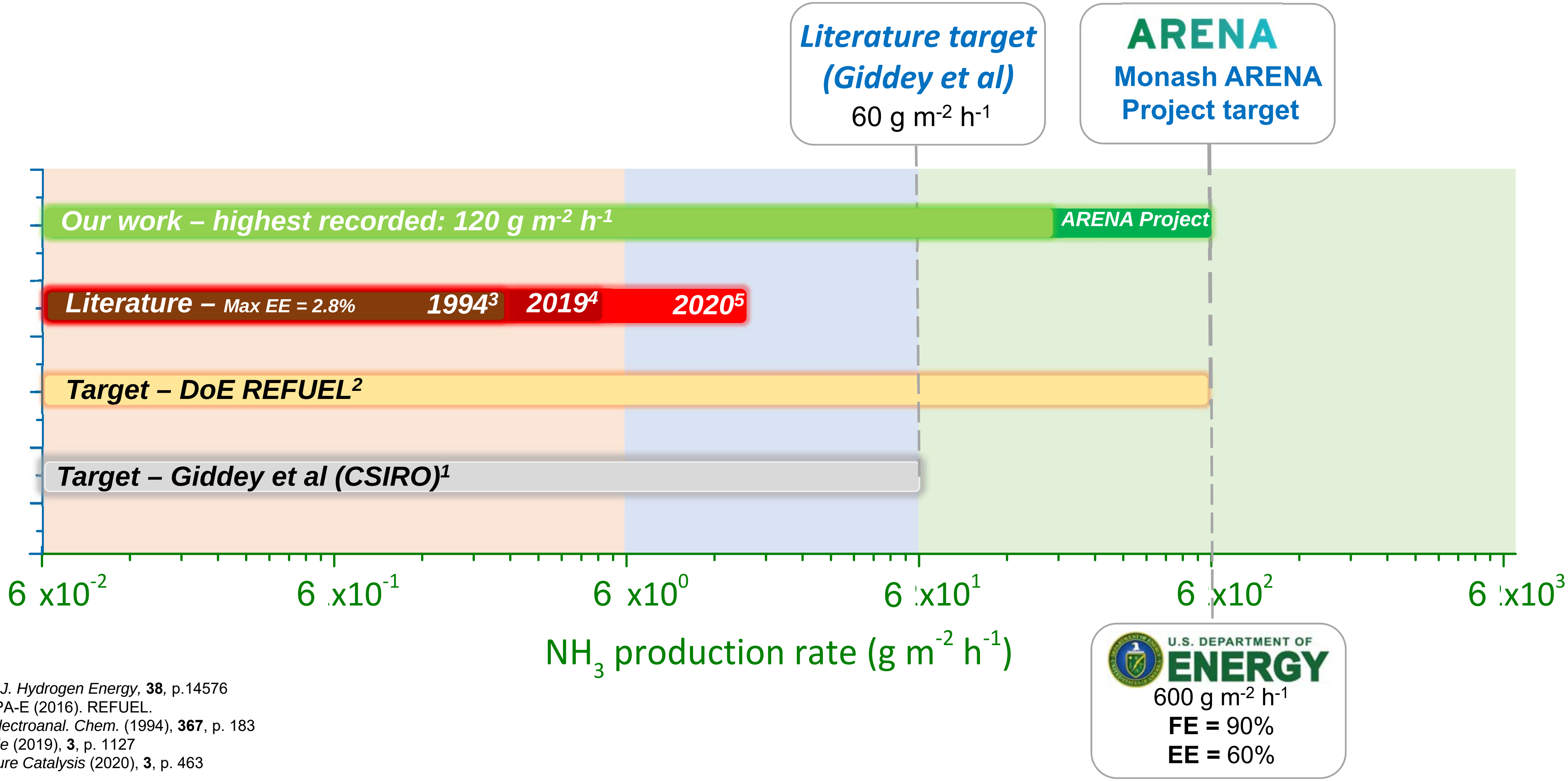
Conventional electrolyte
(0.2 M $LiBF_4$ + 0.17 M EtOH in THF)

Current density : 8 mA cm^{-2}
Cell lifetime : 18 minutes
Cell voltage > 12 V
NH_3 Yield rate : 8.6 g m^{-2} h^{-1}
NH_3 Selectivity : 47.4%

MU-2020

Current density : 22.5 mA cm^{-2}
Test duration > 1200 minutes
Cell voltage < 5 V
NH_3 Yield rate : 43.5 g m^{-2} h^{-1}
NH_3 Selectivity : 92%
Energy efficiency : 25%

ARENA milestones, literature target & performance projection



[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

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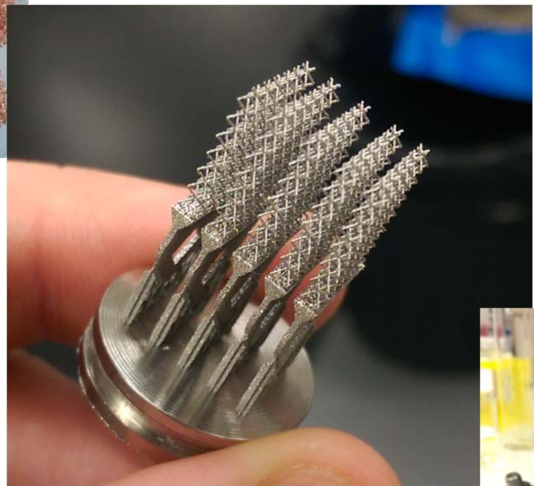

Development of high specific surface area electrodes

- Metal foam
- 3D printed metal electrodes

Prototyping a 1 kW flow cell

Scale-up strategy to further increase production rate

Acknowledgement

The Hydrogen/Ammonia Team

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