High-productivity electrosynthesis of ammonia from dinitrogen

Dr Alexandr (Sasha) N. Simonov

Ammonia Economy Roadmap

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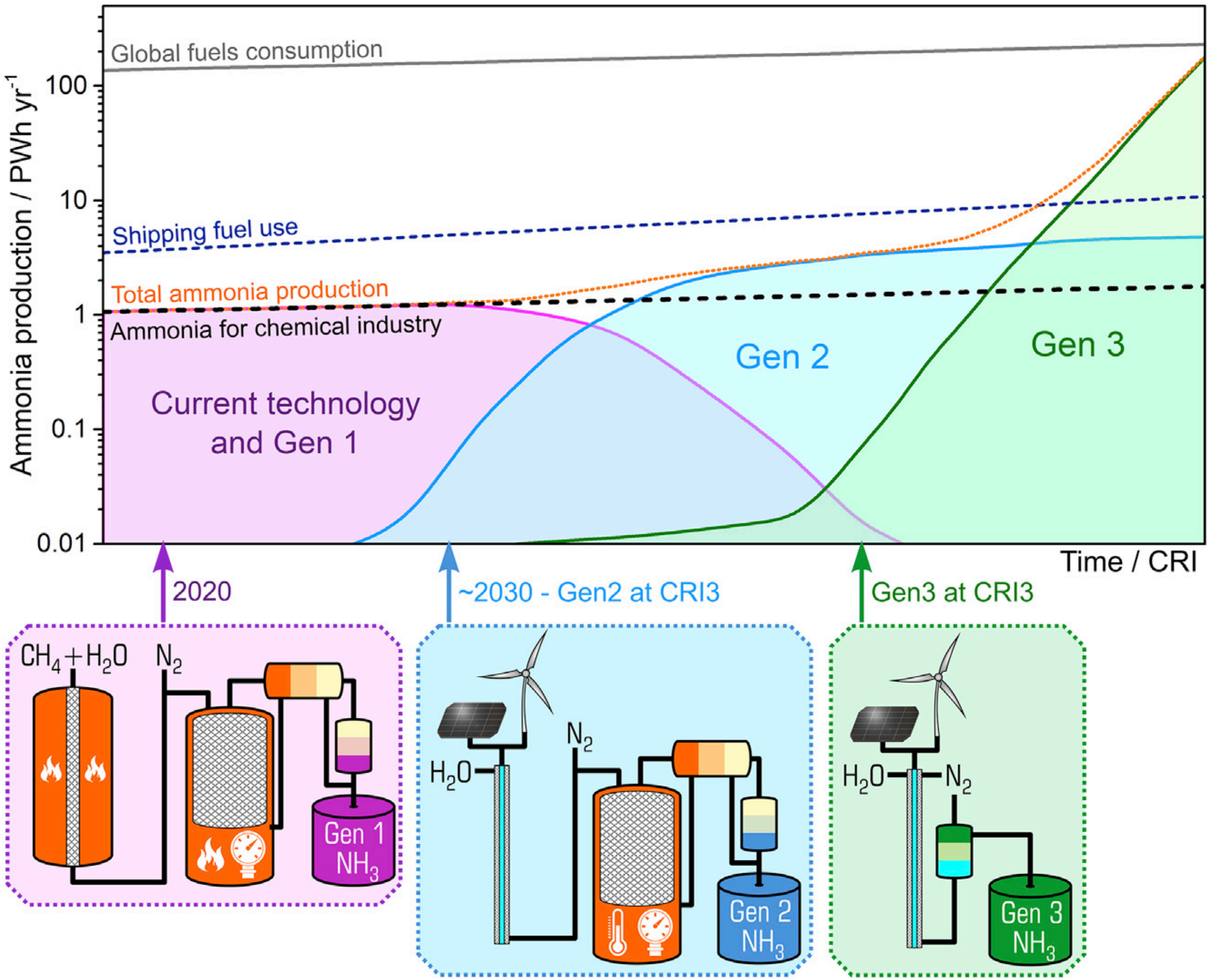
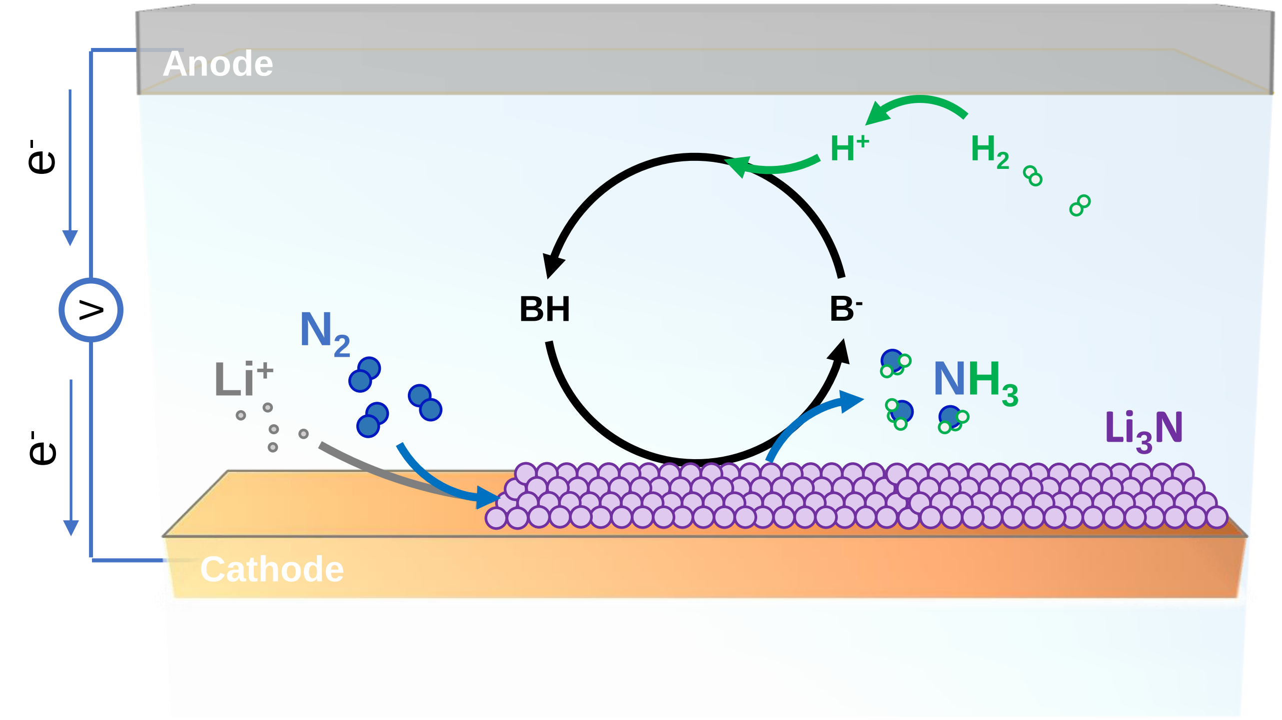


Li-mediated NRR - the one and only



Elektrolytische Bindung von komprimiertem Stickstoff bei gewöhnlicher Temperatur

von **Fr. Fichter, Pierre Girard**[1]) und **Hans Erlenmeyer.**

(27. IX. 30.)

$$Li_3N + 3\,R\cdot OH = 3\,LiOR + NH_3$$

J. Electroanal. Chem **(1994) – 50 bar**
40-60 % at 2 mA cm^{-2}
3-4 nmol s^{-1} cm^{-2}

Joule **(2019) – 1 atm**
9 ± 2 % at 15 mA cm^{-2}
4.5 ± 1.0 nmol s^{-1} cm^{-2}

Nat. Catal. **(2020) – 1 atm**
ca 20 % at 20 mA

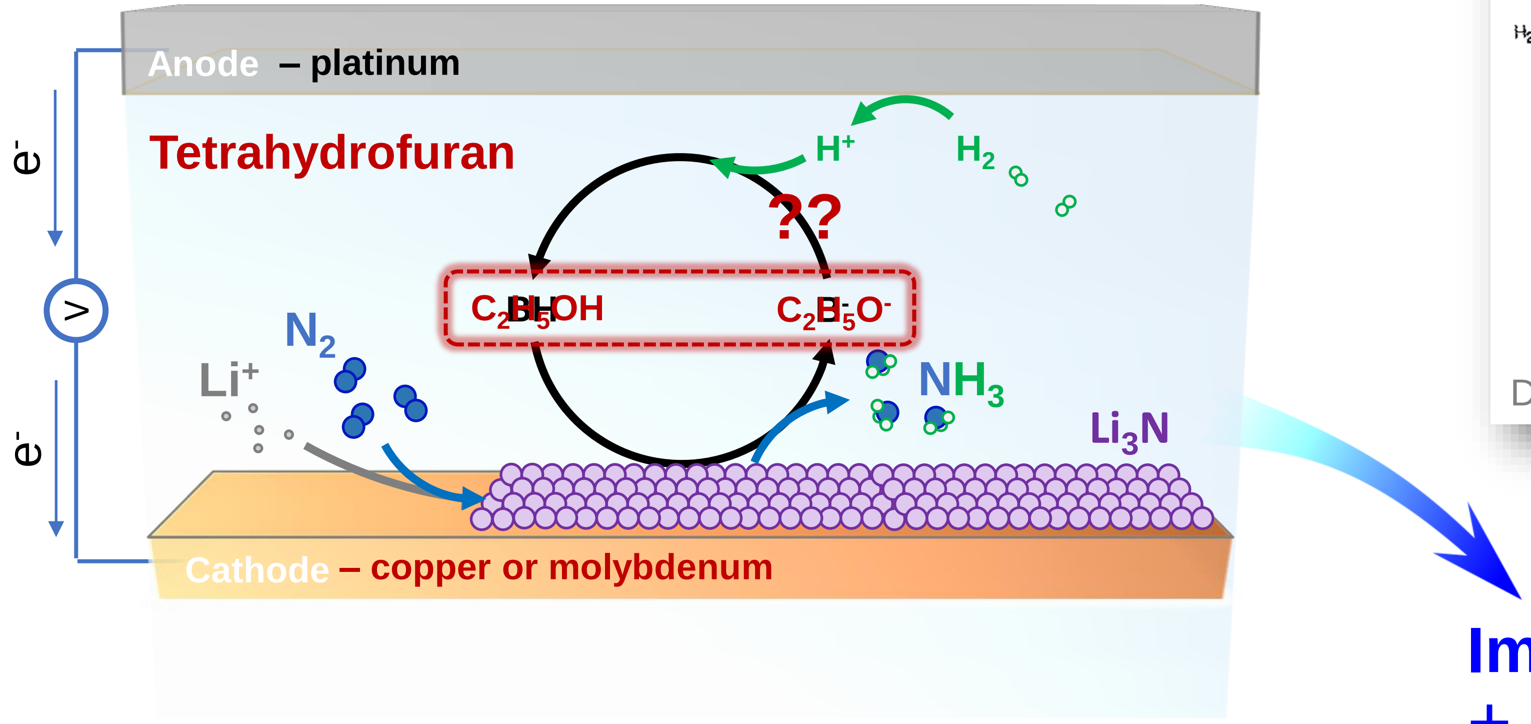
ChemElectroChem **(2020) – 1 atm**
11 ± 1 % at 1 mA cm^{-2}
0.38 ± 0.04 nmol s^{-1} cm^{-2}

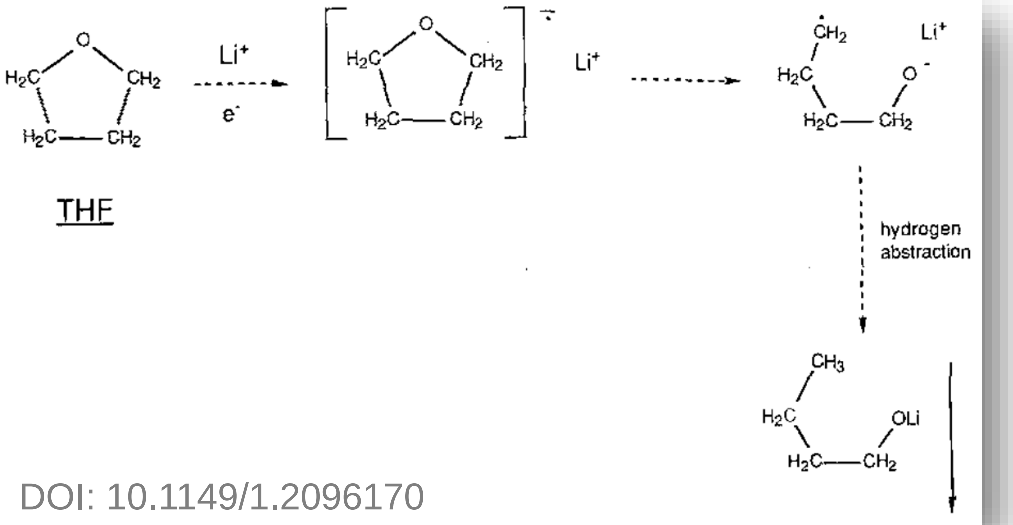
Energy Env. Science **(2020) – 10 bar**
33 ± 1 % at 2 mA cm^{-2} [interrupted regime]
0.25 ± 0.01 nmol s^{-1} cm^{-2}

Angew. Chemie **(2021) – 1 atm**
34 ± 5 % at -4 V *vs.* Pt
0.80 ± 0.02 nmol s^{-1} cm^{-2} at -8 V *vs.* Pt

Improving the Li-mediated NRR system

Since the first detailed investigation of the Li-mediated NRR in 1993, the system has not evolved that much….





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Improving the electrolyte:

+ High ionic conductivity
+ Hydrophobic
+ Chemically stable
+ Non-sacrificial

Advanced proton shuttle

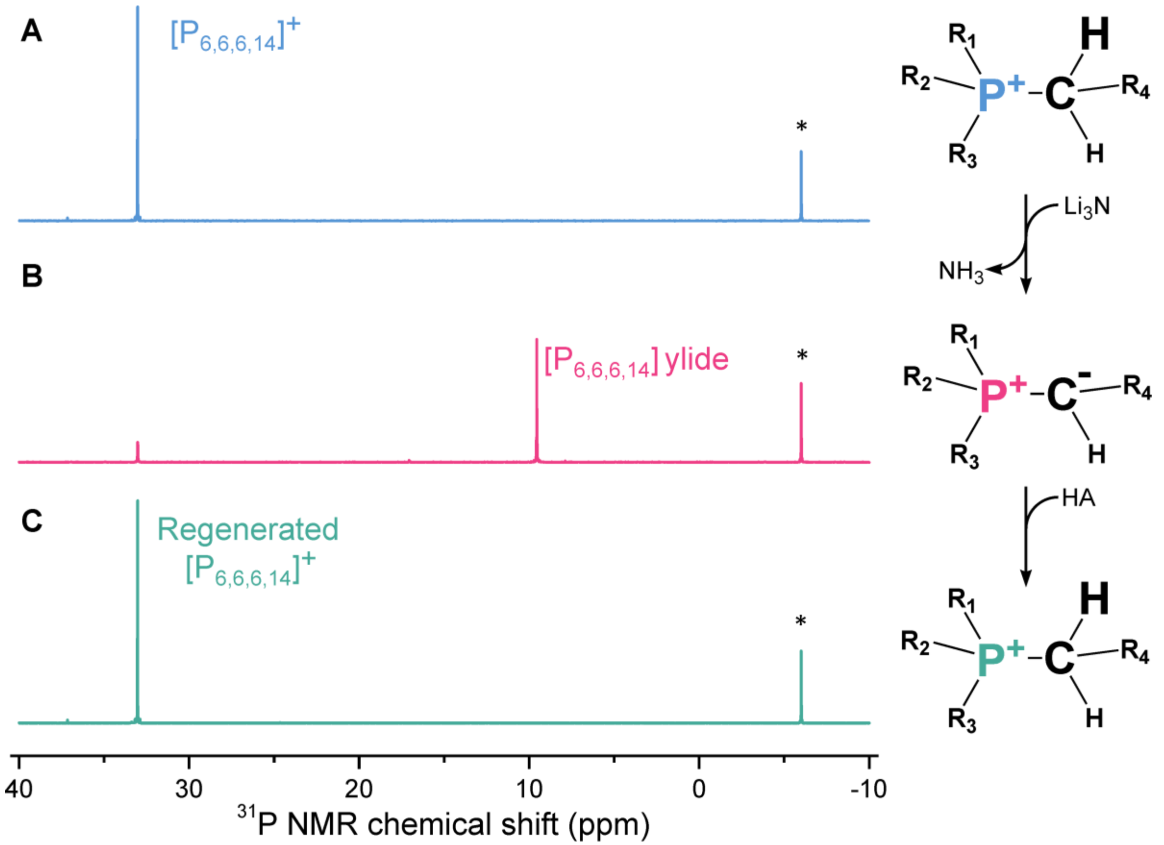
RESEARCH

10.1126/science.abg2371

ELECTROCHEMISTRY

Nitrogen reduction to ammonia at high efficiency and rates based on a phosphonium proton shuttle

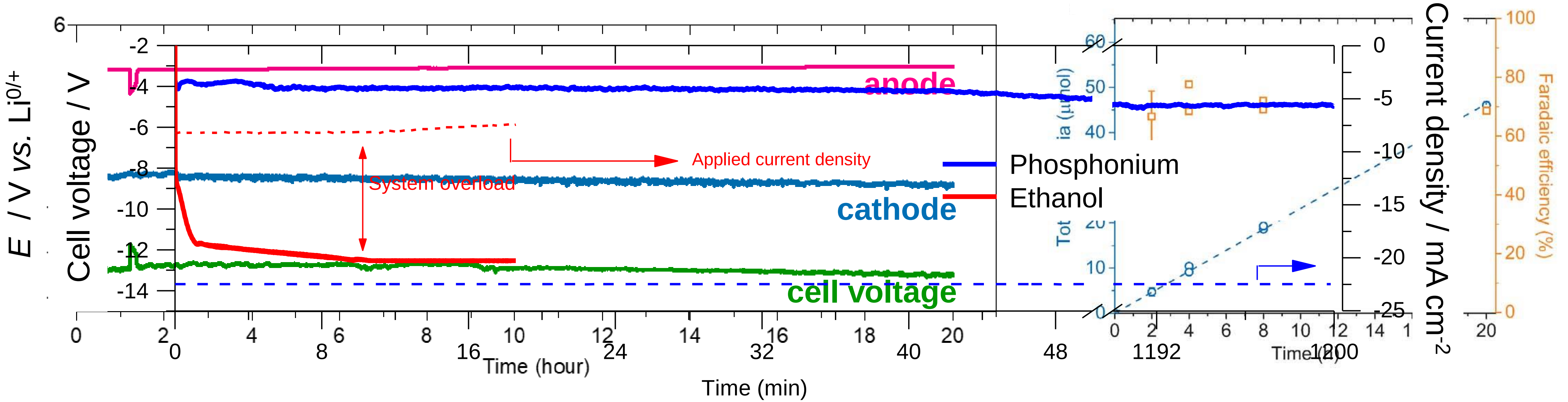
Bryan H. R. Suryanto[1]*, Karolina Matuszek[1], Jaecheol Choi[1,2], Rebecca Y. Hodgetts[1,2], Hoang-Long Du[1,2], Jacinta M. Bakker[1,2], Colin S. M. Kang[1,2], Pavel V. Cherepanov[1], Alexandr N. Simonov[1,2]*, Douglas R. MacFarlane[1,2]*



MONASH CHEMISTRY

Phosphonium *vs.* ethanol

Performance in $N_2 + H_2$ < than in pure N_2 due to $Li^0 + ½H_2 \rightarrow LiH$



C_2H_5OH

Current density	8 mA cm^{-2}
Cell lifetime	**18 minutes**
Cell voltage	**> 12 V**
NH_3 Yield rate	**14 nmol s^{-1} cm^{-2}**
Faradic efficiency	**47%**

$[P_{6,6,6,14}][eFAP]$

Current density	22.5 mA cm^{-2}
Test duration	**>20 h**
Cell voltage	**<5 V**
NH_3 Yield rate	**53 ± 1 nmol s^{-1} cm^{-2}**
Faradic efficiency	**69 ± 1 %**
Energy efficiency	up to 22%

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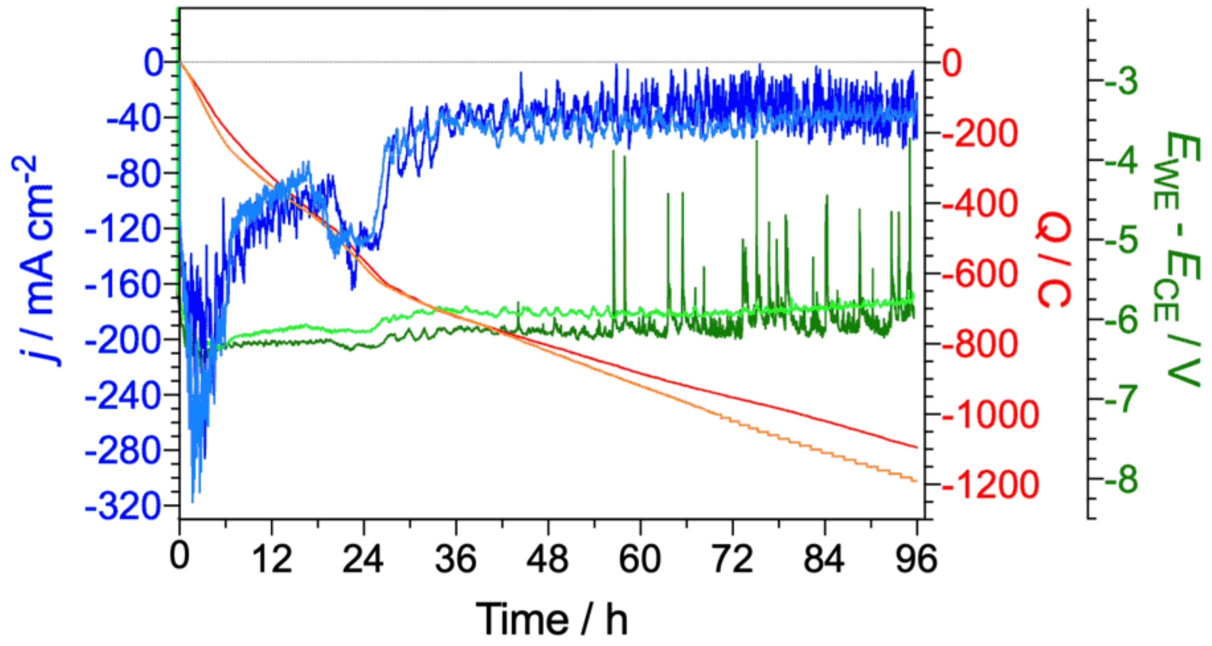
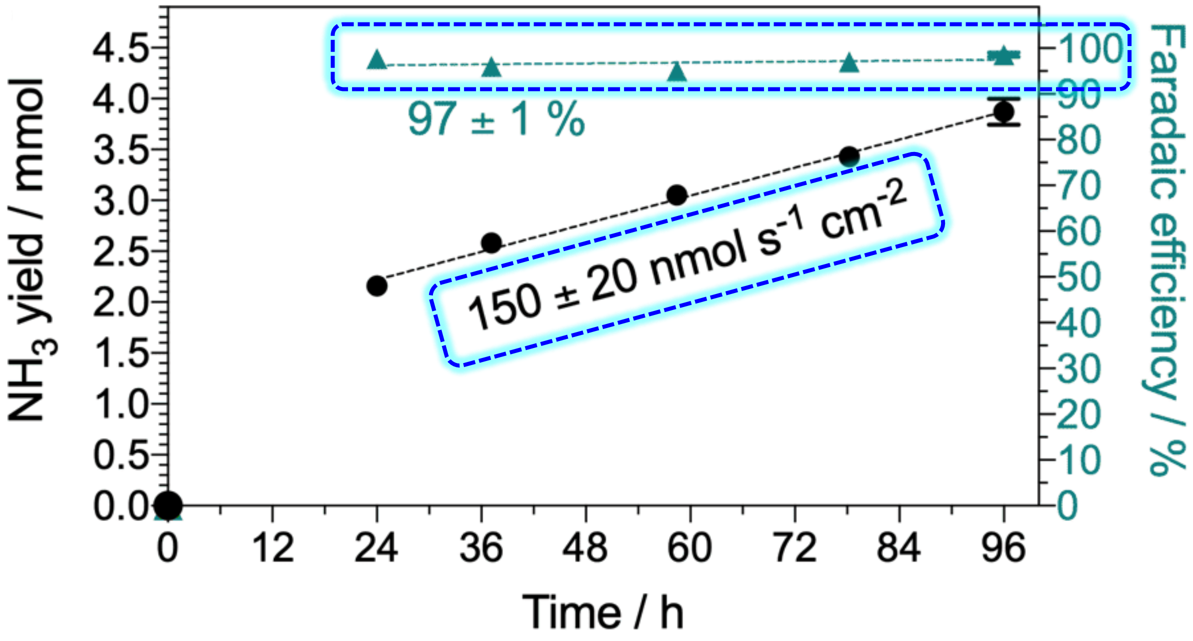
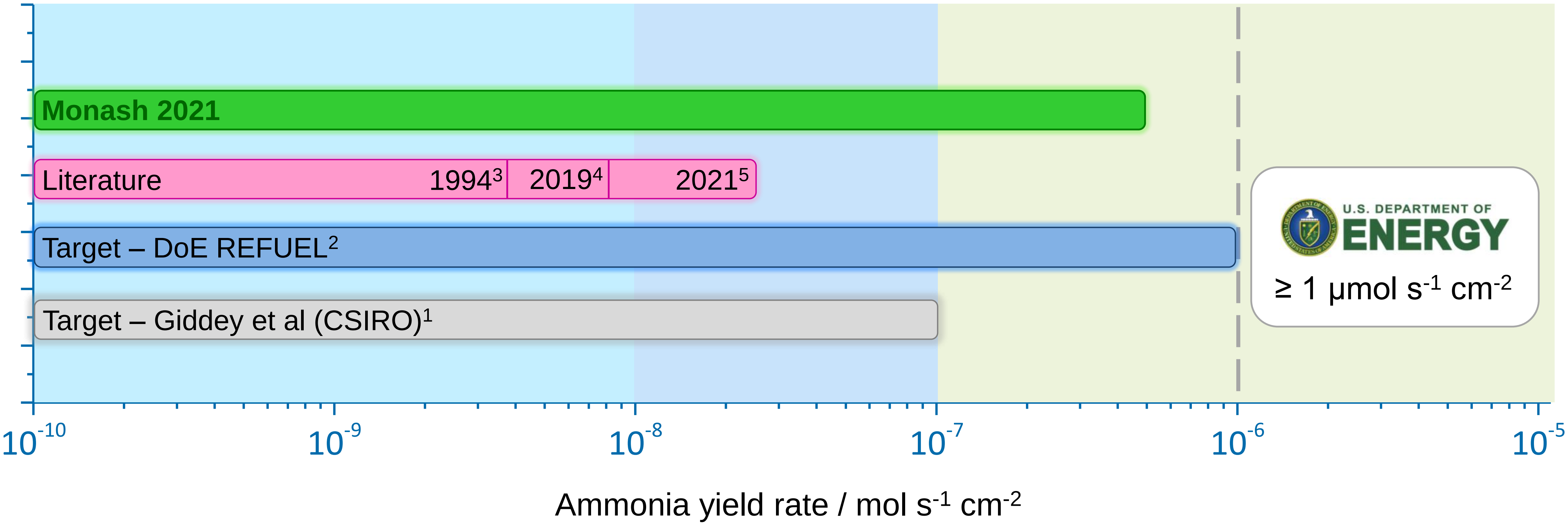
New electrolyte compositions

Operation at a constant potential of -0.55 V *vs.* $Li^{0/+}$



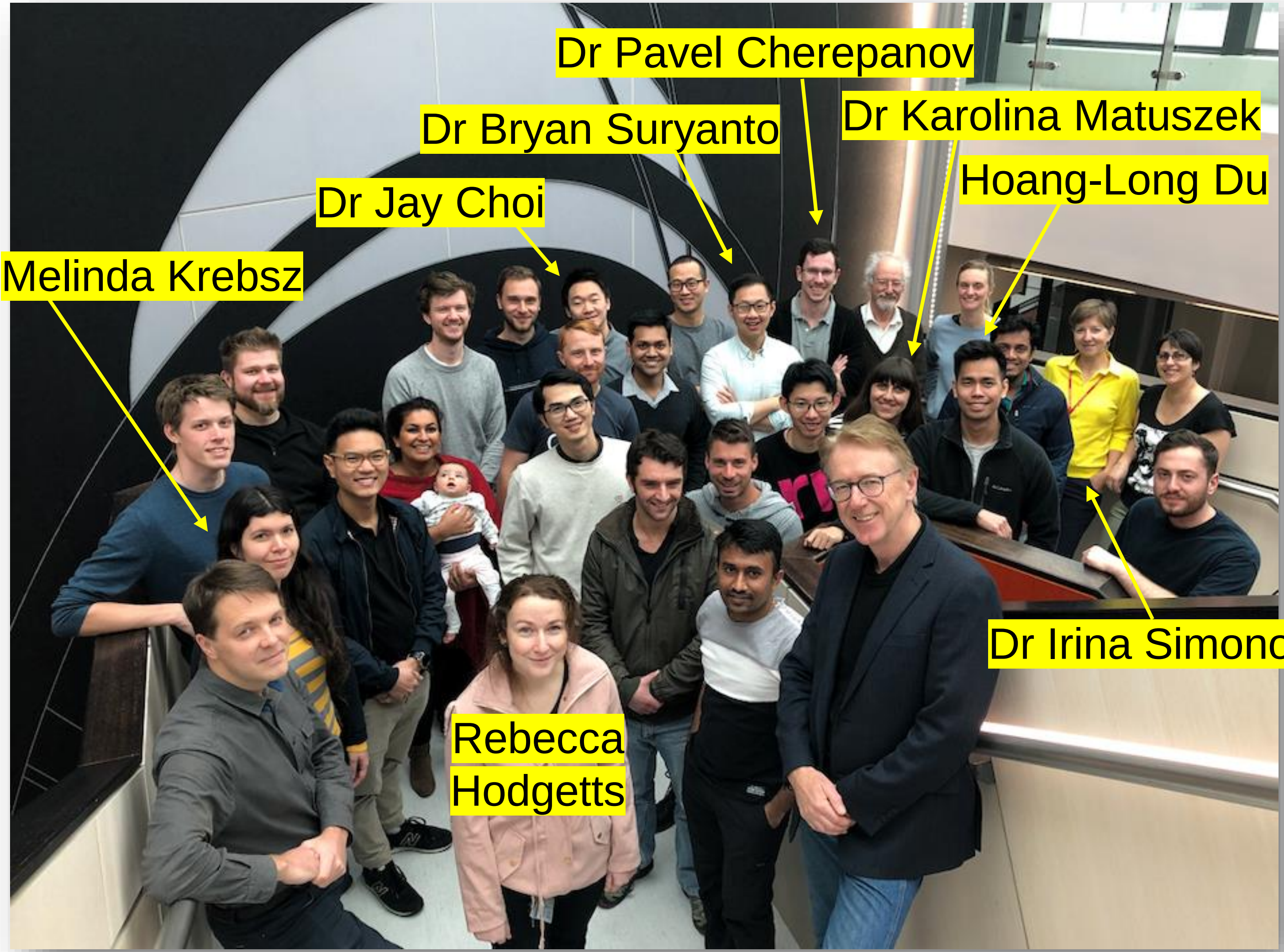


Milestones



[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

Acknowledgements



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