ARC Centre of Excellence for Electromaterials Science

MONASH University

Whither Aqueous Electro-reduction of Nitrogen to Ammonia?

or

Doug MacFarlane

Monash University

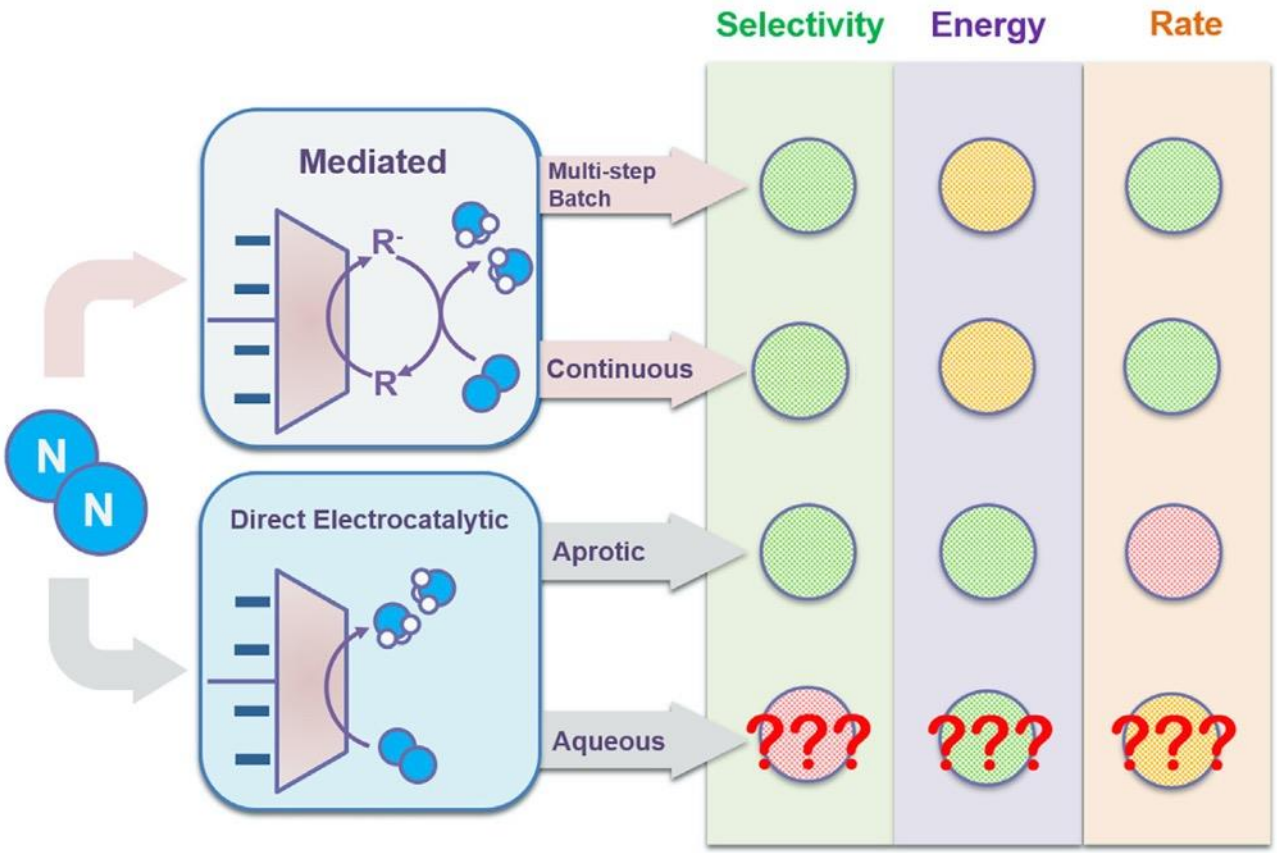
Australian Government
Australian Research Council

Australian Academy of Science

Australian Government
Australian Renewable Energy Agency

ARENA

Approaches to Ambient Temperature N_2 --> NH_3



MacFarlane et al *Joule* 2020

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Aqueous NRR – Current Status

Many reports……*but!!!*

- Selectivity rarely > 20% (not practical versus Gen 2)
- Yields so low => prone to false positives
- Often using huge volumes of N_2 gas
  => very small amounts of Nox's problematical
- Papers are now being refuted:
  - Du et al. *ACS Sust Chem. Eng.* 2019.
  - Hu et al. *ACS Energy Lett.* 2019 & Editor's Commentary
  - Has et al *Nature Cat* 2019 Matters Arising 2020
  - Choi et al *Nature Comms* 2020

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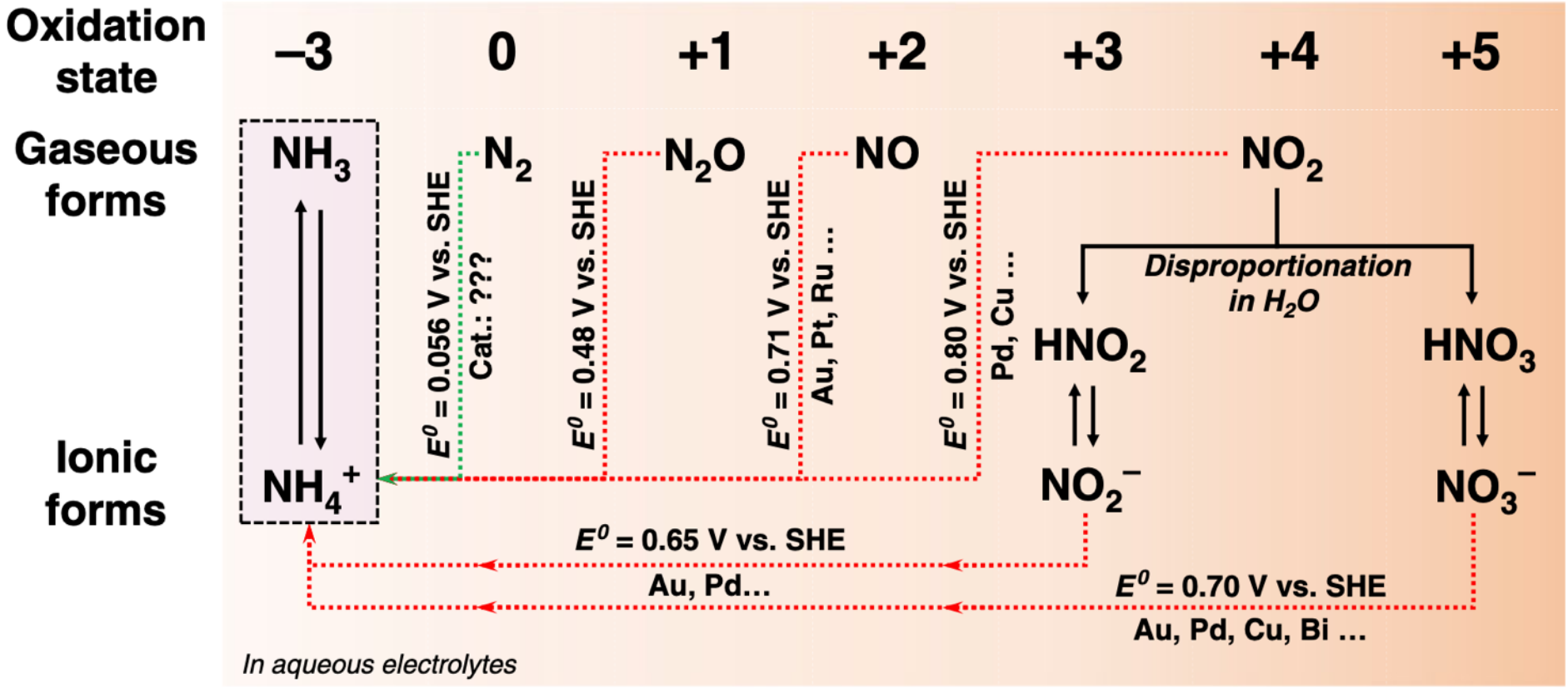
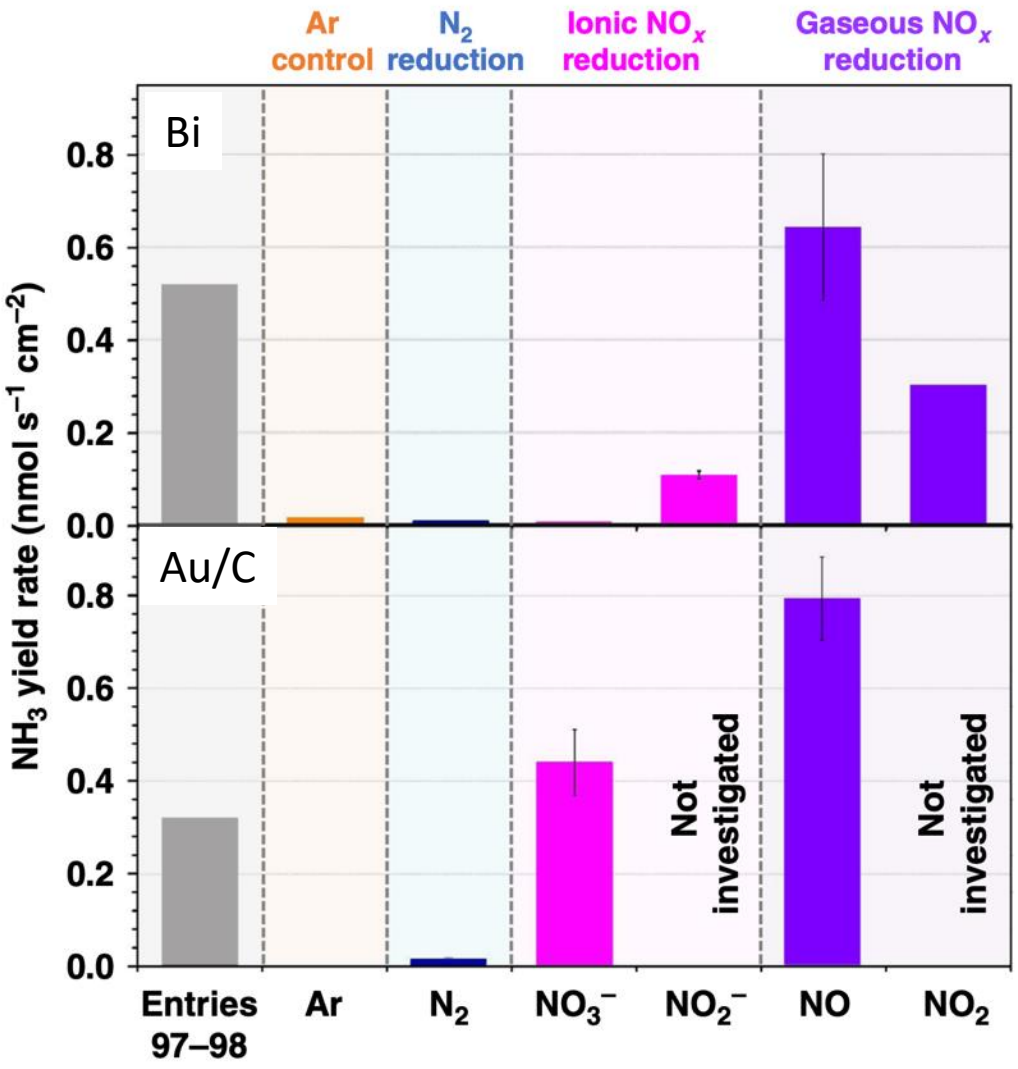
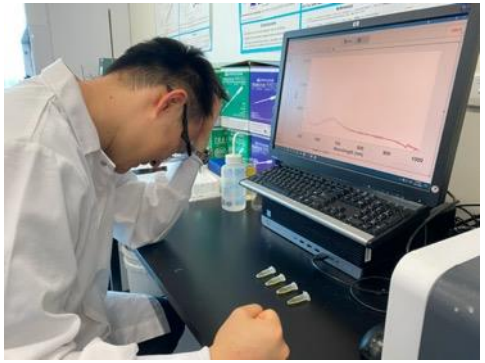
The "Richness" of Nitrogen Chemistry!



Choi et al *Nat Comm* 2020
Choi et al *ACS Energy Letters* 2020

=> Frustratingly False Positives!





A very frustrated Jay Choi

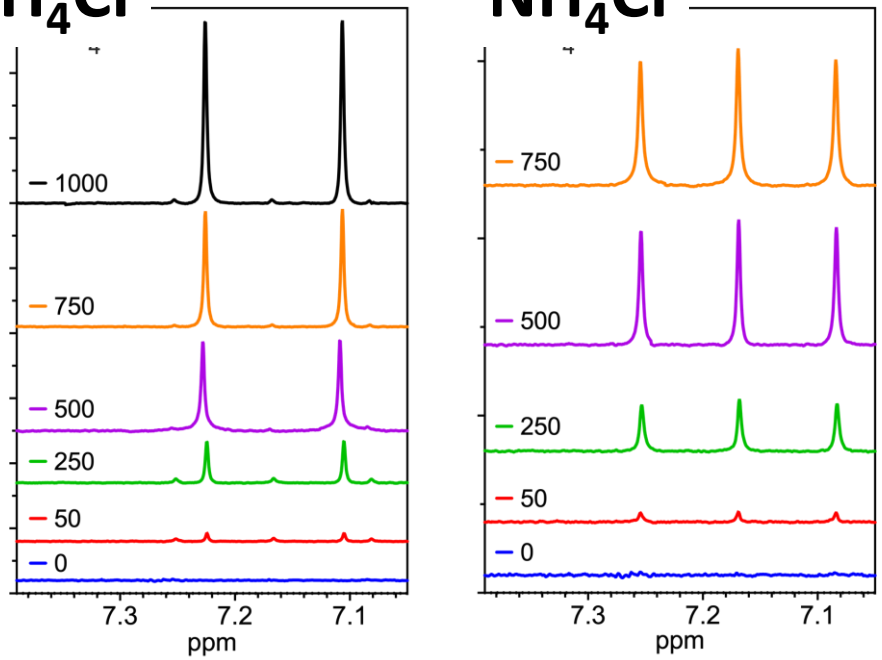
Choi et al *Nat Comm* 2020

$^{15}N_2$ studies important to prove NRR……

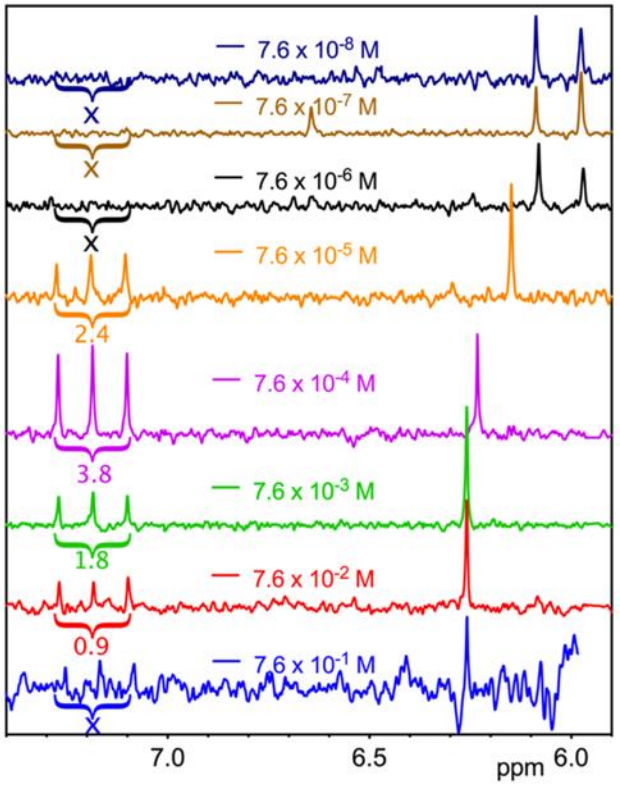
……..but not foolproof

The difference is clear in the ^{1}H NMR:

$^{15}NH_4Cl$ $^{14}NH_4Cl$



But it depends critically on conditions
Eg pH:



Hodgetts et al ACS Energy Lett 2020

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A Traffic Light Analysis of Literature

No.	Year	Material	N-based material	Electrolyte	*E* (V vs. RHE)	FE (%)	Yield rate (nmol s^{-1} cm^{-2})	Quantitative $^{15}N_2$ test	NO_x control	Ref.
19	2018	Fe/Fe_3O_4	N	0.1 M PBS	-0.3	8.3	0.003	N	N	19
20	2018	Ag	N	0.1 M HCl	-0.6	4.8	0.046	N	N	20
21	2018	C	N	0.1 M Na_2SO_4	-0.3	6.9	0.26	N	N	21
22	2018	NbO_2	N	0.05 M H_2SO_4	-0.65	20	0.19	N	N	22
23	2018	Y_2O_3	N	0.1 M Na_2SO_4	-0.9	2.5	0.11	N	N	23
24	2018	d-MoS_2	Y	0.1 M Na_2SO_4	-0.4	8.3	0.19	N	N	24
25	2018	Au/CN_x	Y	0.1 M HCl	-0.2	12	0.038	N	N	25
26	2018	Au/C_3N_4	Y	0.005 M H_2SO_4	-0.1	11	0.031	N	N	26
27	2018	Fe/N-CNT	Y	0.1 M KOH	-0.2	9.3	0.29	N	N	27
28	2018	B-TiO_2	N	0.1 M Na_2SO_4	-0.8	3.4	0.024	N	N	28
29	2018	B_4C	N	0.1 M HCl	-0.75	16	0.043	N	N	29
30	2018	Au	N	0.1 M HCl	-0.2	6.1	0.25	N	N	30
31	2018	Mn_3O_4	N	0.1 M Na_2SO_4	-0.8	3.0	0.038	N	N	31
32	2018	CN_x	N	0.1 M HCl	-0.2	1.5	1.0	N	N	32
33	2018	SnO_2	N	0.1 M Na_2SO_4	-0.8	1.2	0.15	N	N	33
34	2018	TiO_2	N	0.1 M Na_2SO_4	-0.7	2.5	0.092	N	N	34
35	2018	VN	N	0.05 M H_2SO_4	-0.2	6.5	0.50	N	N	35

- Choi et al *Nature Comms* 2020

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Experimental Set-up & Protocols

Conclusion:

- Gas purification and analysis vital:

- H_2O (in aprotics)
- Nitrate/nitrite
- NO_x (all of them)
- NH_3

- See latest protocol commentary in Choi et al *Nat Comm* 2020

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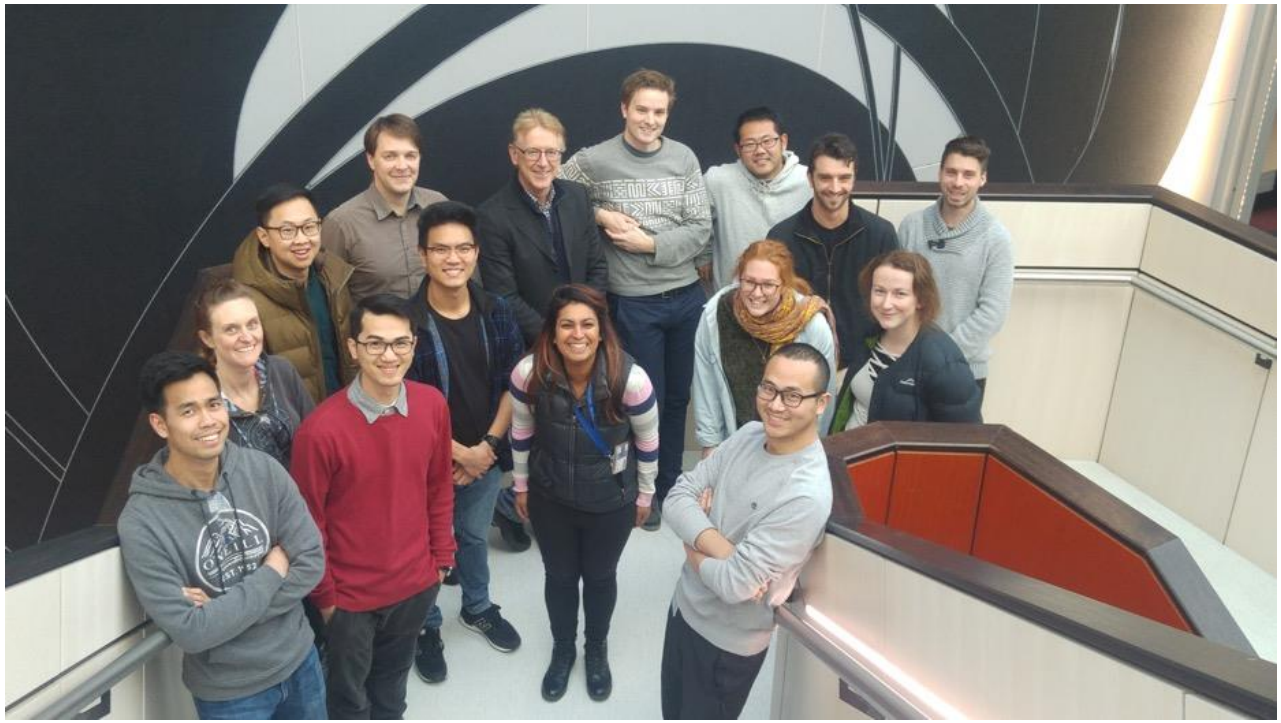
Acknowledgement$$

The Hydrogen/Ammonia Team



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