High Efficiency Ammonia Electrosynthesis via Understanding the Mass-transport Effects of Phosphonium Ionic Liquids

Trung Nguyen [a], Hoang-Long Du [a], Luke A. O'Dell [b], Alexandr N. Simonov [a,*], Douglas R. MacFarlane [a,*]

[a] *ARC Center of Excellence for Electromaterials Science, School of Chemistry, Monash University, Clayton, Victoria 3800, Australia*

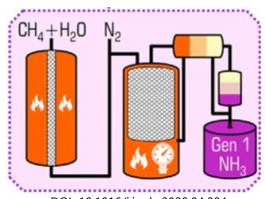
[b] *Institute for Frontier Materials, Deakin University, Geelong, Victoria 3216, Australia*

Email: trung.nguyen3@monash.edu

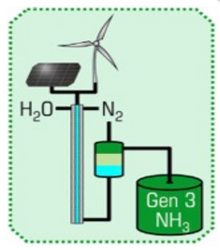
Introduction

Conventional Haber-Bosch process

- Intensive resource and energy consumption
- Contribute ~2% of global CO_2 emissions



DOI: 10.1016/j.joule.2020.04.004

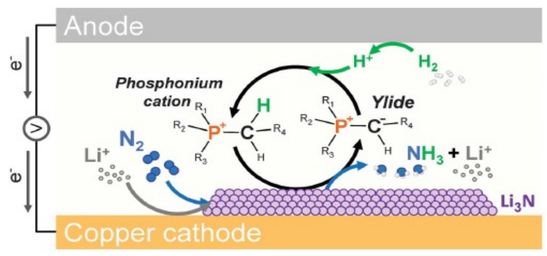


DOI: 10.1016/j.joule.2020.04.004

NH_3 electrosynthesis

- Allow to occur under mild ambient conditions
- Green & zero emission
- Powered by renewable energy

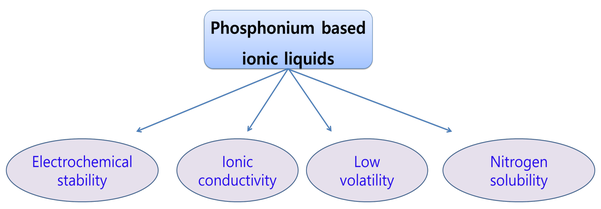
N_2 and H_2O can be converted into NH_3 via electrochemical process enabled by renewable electricity



DOI: 10.1126/science.abg2371

Li-mediated nitrogen reduction (Li-NRR): the most promising way to synthesize NH_3 with high faradaic efficiency and prospective rates.

- Common proton carrier: **Ethanol** $\quad Li_3N + 3\,H^+ \rightarrow 3\,Li^+ + NH_3$
- Alternative: **Phosphonium-based ionic liquids** with unique properties

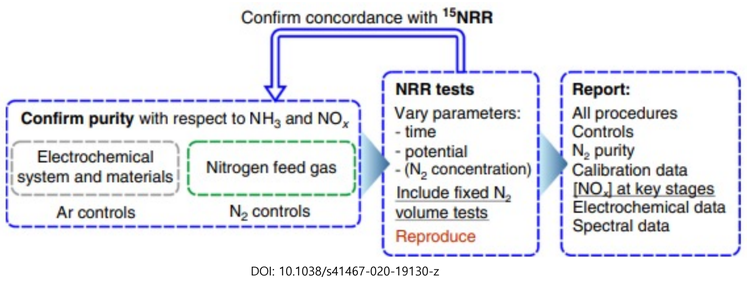


Objectives

- Investigation of the mass-transport effects of phosphonium-based ionic liquids
- Designing an effective continuous flow cell to study mass-transport in the Li-NRR system
- Kinetic modelling and simulation for discovering mechanistic insight for the Li-NRR

Experimental

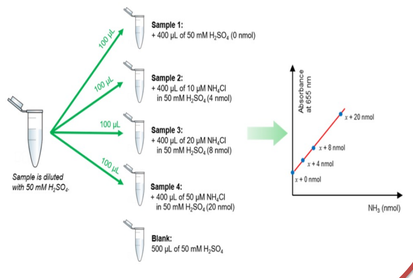
Electrochemical and control procedure



DOI: 10.1038/s41467-020-19130-z

Ammonia quantification: Spectrophotometric Berthelot method

- Standard addition method: eliminate matrix interferences
- Ammonia concentrations correspond to absorbance of indophenol chromophore



DOI: 10.1126/science.abg2371

Phosphonium Proton Shuttle for the NRR

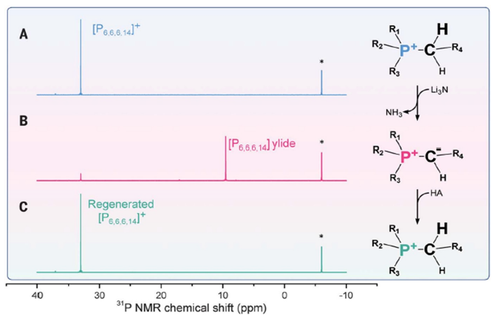
Science

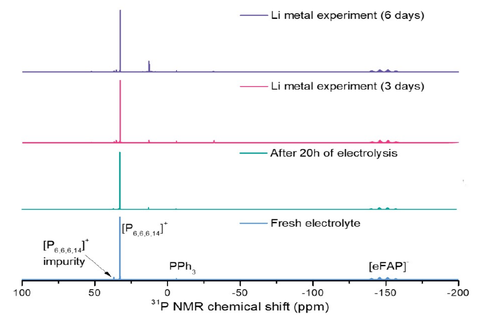
Nitrogen reduction to ammonia at high efficiency and rates based on a phosphonium proton shuttle

Bryan H. R. SuryantoKarolina MatuszekJaecheol ChoiRebecca Y. HodgettsHoang-Long DuJacinta M. BakkerColin S. M. KangPavel V. CherepanovAlexandr N. SimonovDouglas R. MacFarlane

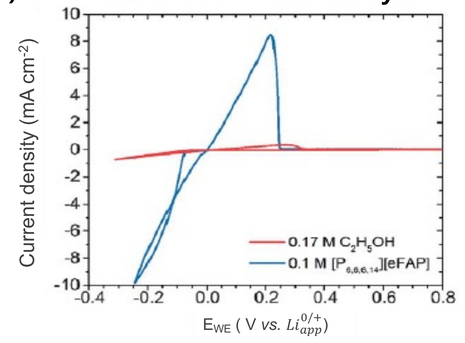
- ✓$[P_{6,6,6,14}][eFAP]$: a stable proton shuttle for Li-NRR
- ✓NH_3 yield rate ~ 53 ± 1 nmol s^{-1} cm^{-2} ; Faradaic efficiency ~ 69 ± 1 % in 20h under 19.5 bar N_2 & 0.5 bar H_2
- ✓Continuous operation is successfully conducted in 3 days

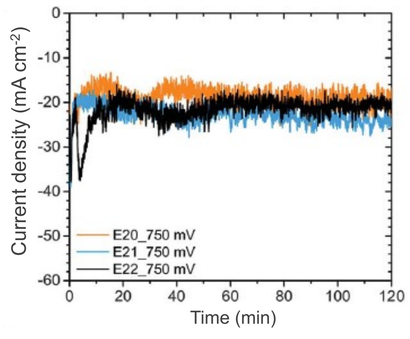
Cyclic transformation of phosphonium IL (^{31}P NMR)



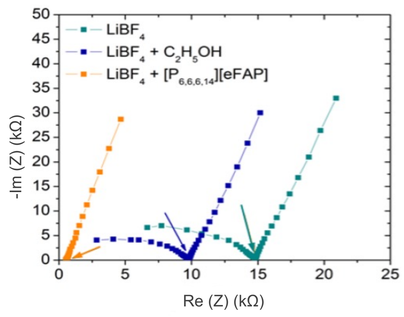


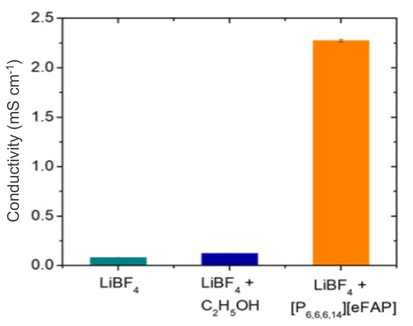
Electrochemical analysis

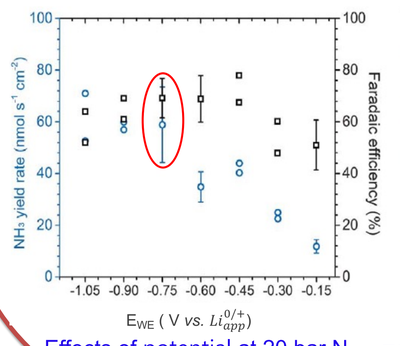




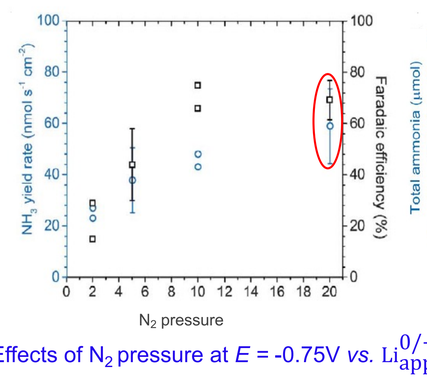
Reduction rate increased 10 times



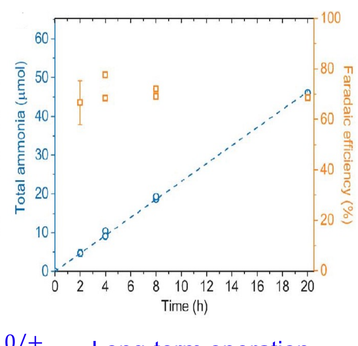


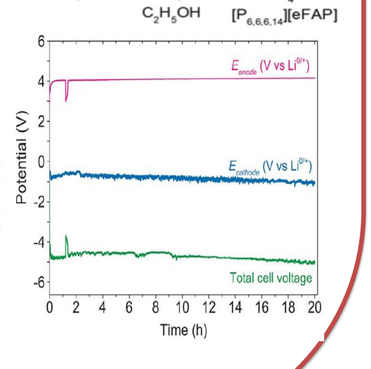


Effects of potential at 20 bar N_2



Effects of N_2 pressure at E = -0.75V *vs.* $Li^{0/+}_{app}$

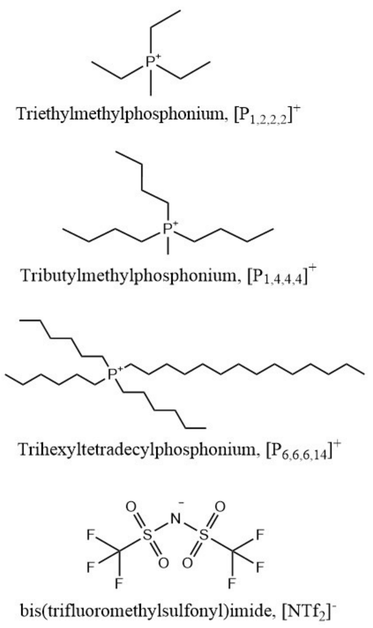




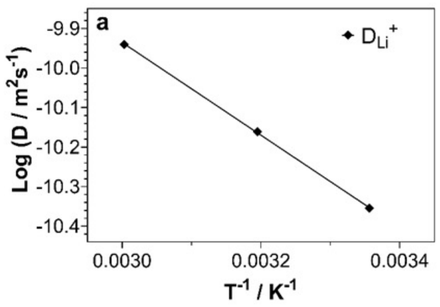
Long-term operation

Improved Phosphonium Proton Shuttle

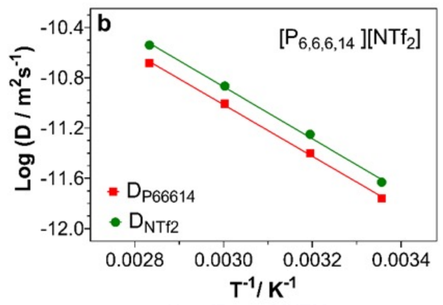
New phosphonium-based ionic liquids as proton shuttles for the NRR



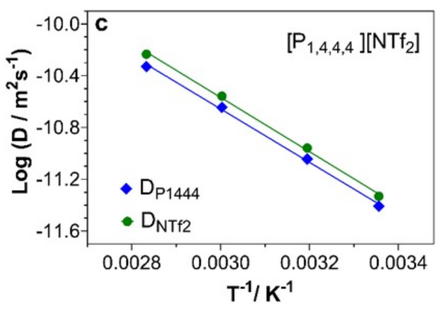
Diffusion coefficients of Li^+ and phosphonium cations in the electrolyte solution



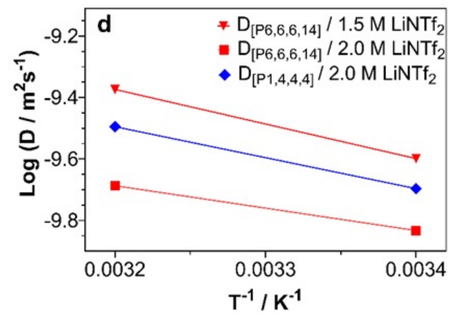
2.5 M $LiNTf_2$ in THF solvent



Neat $[P_{6,6,6,14}]$ $[NTf_2]$

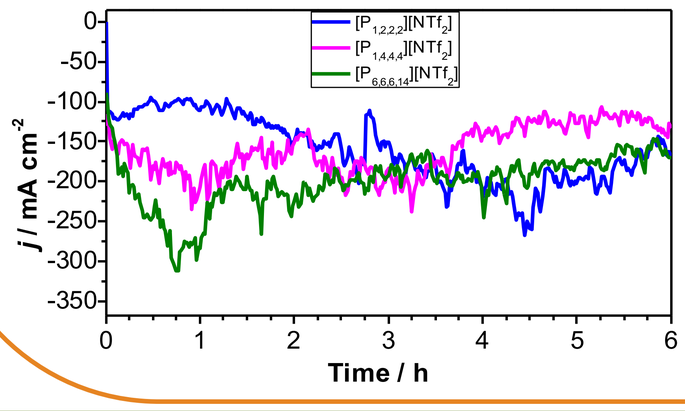


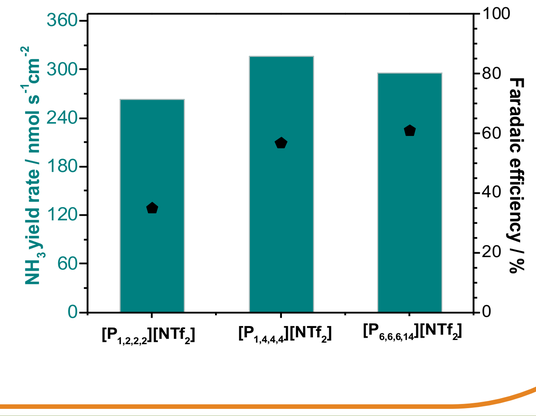
Neat $[P_{1,4,4,4}]$ $[NTf_2]$



0.1 M ILs in $LiNTf_2$ / THF electrolyte

Lithium-mediated NRR performance





REFERENCES

1. MacFarlane, D. R.; Cherepanov, P. V.; Choi, J.; Suryanto, B. H. R.; Hodgetts, R. Y.; Bakker, J. M.; Ferrero Vallana, F. M.; Simonov, A. N., A Roadmap to the Ammonia Economy. *Joule* **2020,** *4* (6), 1186-1205.
2. Suryanto, B. H. R.; Matuszek, K.; Choi, J.; Hodgetts, R. Y.; Du, H.-L.; Bakker, J. M.; Kang, C. S. M.; Cherepanov, P. V.; Simonov, A. N.; MacFarlane, D. R., Nitrogen reduction to ammonia at high efficiency and rates based on a phosphonium proton shuttle. *Science* **2021,** *372* (6547), 1187-1191.
3. Choi, J.; Suryanto, B. H. R.; Wang, D.; Du, H.-L.; Hodgetts, R. Y.; Ferrero Vallana, F. M.; MacFarlane, D. R.; Simonov, A. N., Identification and elimination of false positives in electrochemical nitrogen reduction studies. *Nature Communications* **2020,** *11* (1), 5546.
4. Lazouski, N.; Steinberg, K. J.; Gala, M. L.; Krishnamurthy, D.; Viswanathan, V.; Manthiram, K., Proton Donors Induce a Differential Transport Effect for Selectivity toward Ammonia in Lithium-Mediated Nitrogen Reduction. *ACS Catalysis* **2022**, 5197-5208.