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Electrochemical Ammonia Synthesis Under Ambient Conditions

NEDO Research and Development Program for Promoting Innovative Clean Energy Technologies Through International Collaboration

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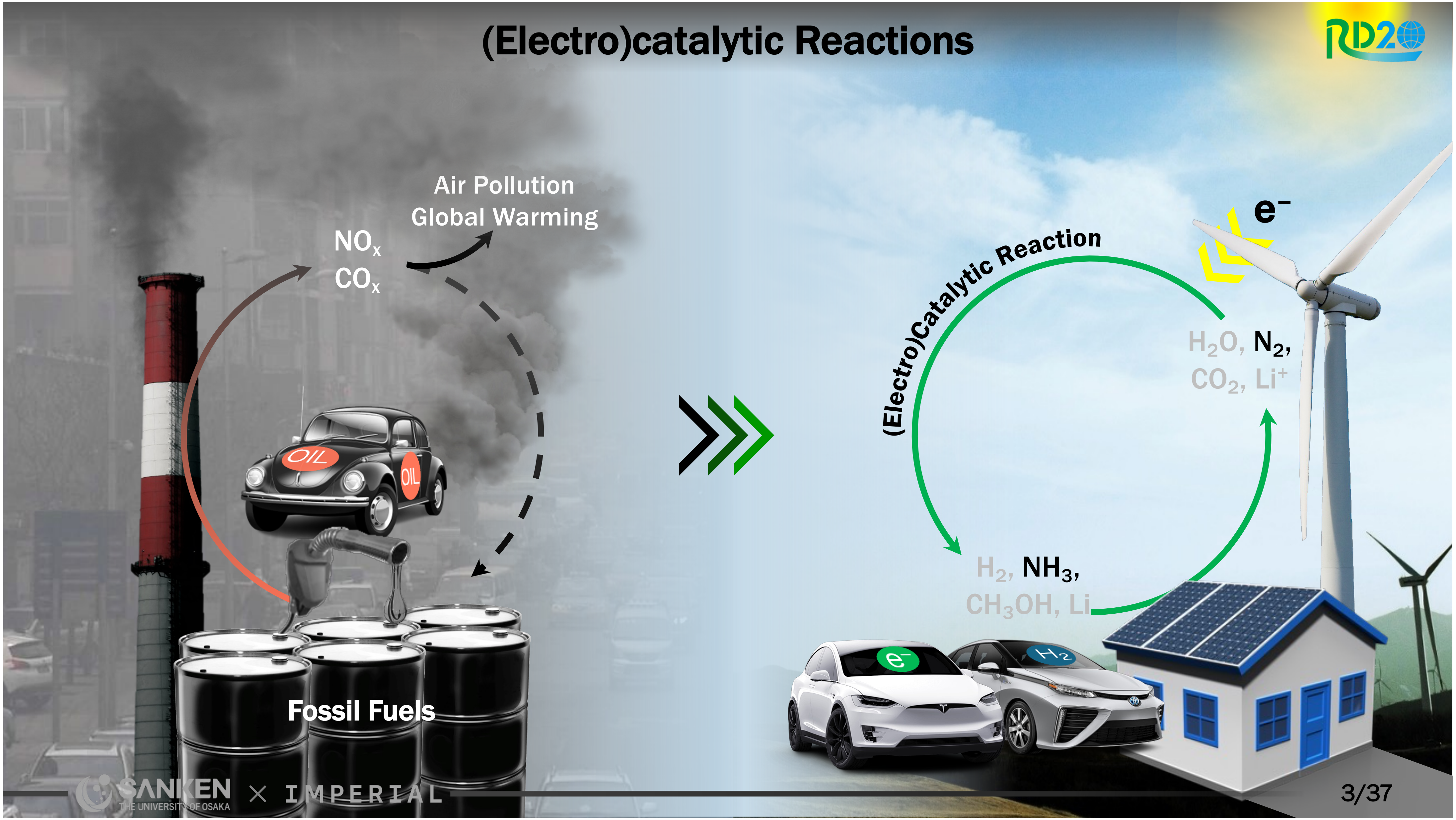
(Electro)catalytic Reactions
RD20
Air Pollution
Global Warming
NO$_x$
CO$_x$
OIL
OIL
Fossil Fuels
(Electro)Catalytic Reaction
e$^-$
H$_2$O, N$_2$,
CO$_2$, Li$^+$
H$_2$, NH$_3$,
CH$_3$OH, Li
e$^-$
H$_2$
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× IMPERIAL
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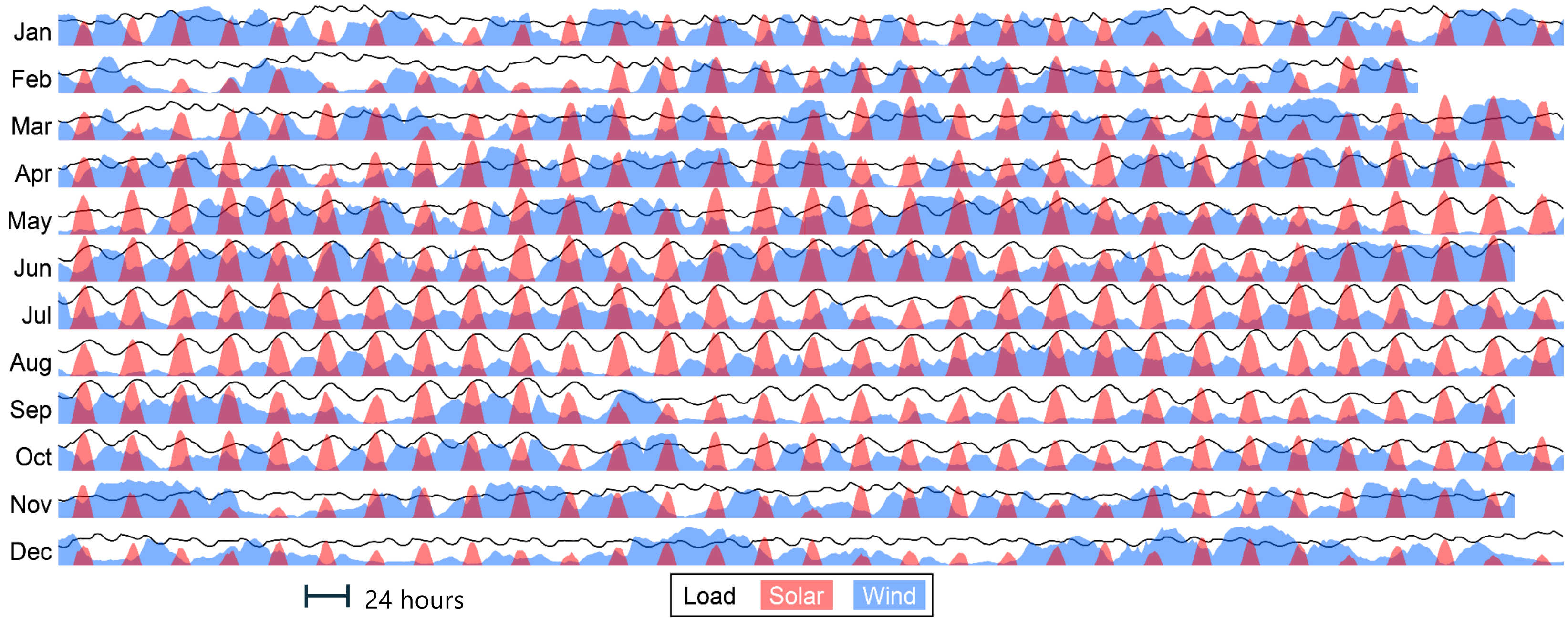
Renewable Energy Sources

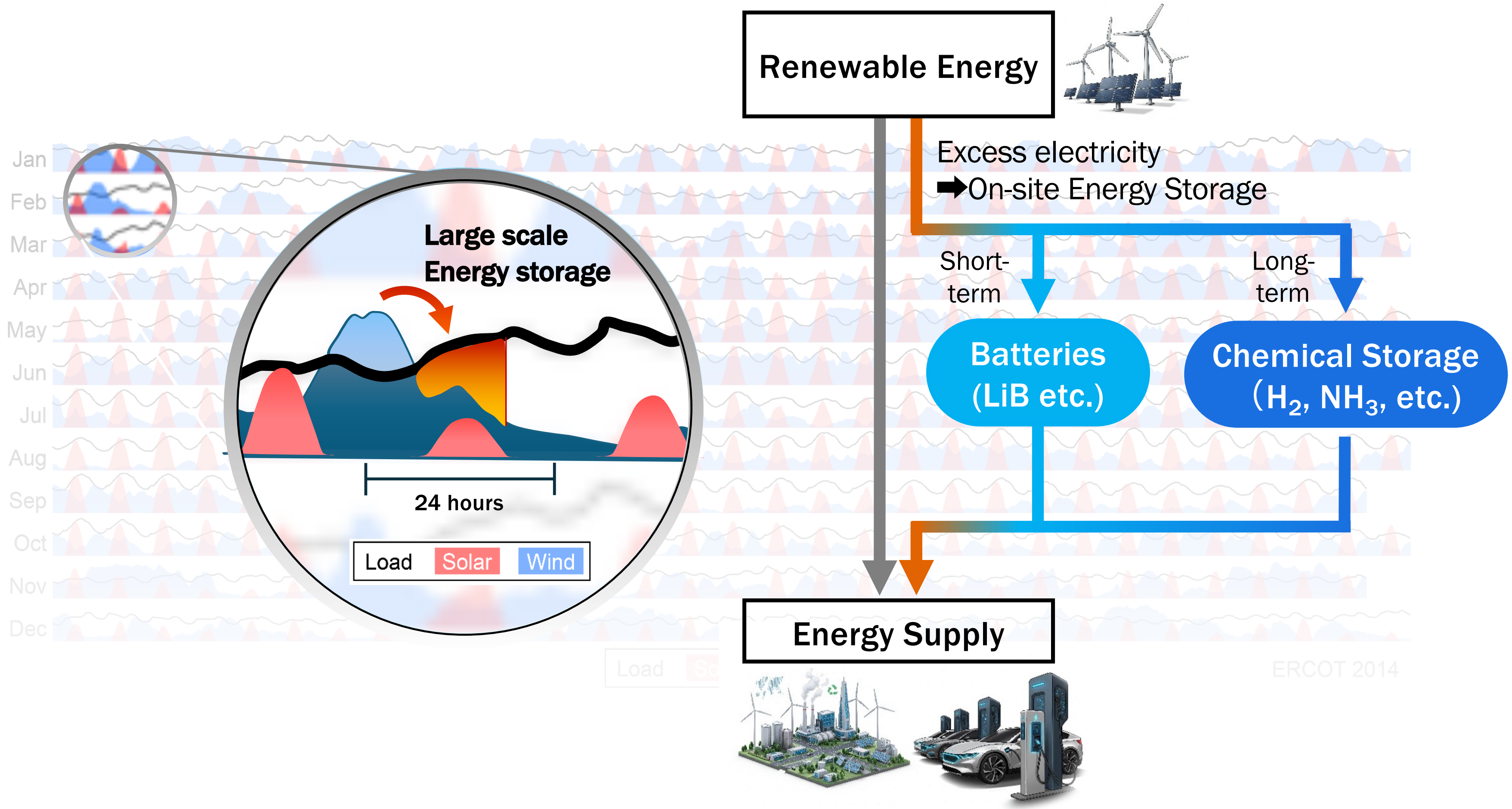
Daily variability of wind and solar resource in Texas relative to load in 2014



Clean and Sustainable, but Intermittent

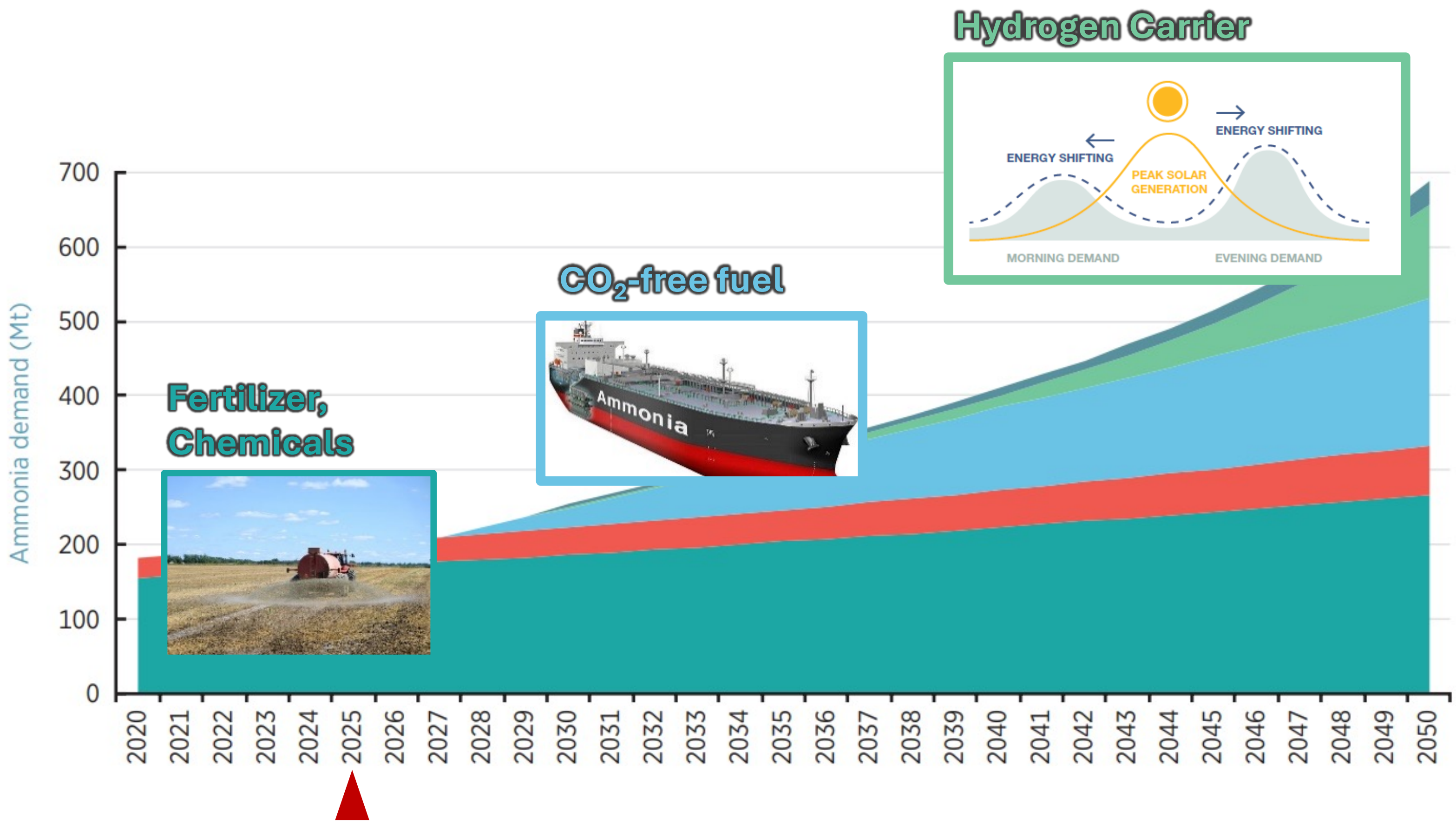
Source: MIT Analysis, NSRDB, ERCOT, P. Brown

Large Scale Energy Storage Systems



Why Ammonia? –Ammonia Demand Forecast

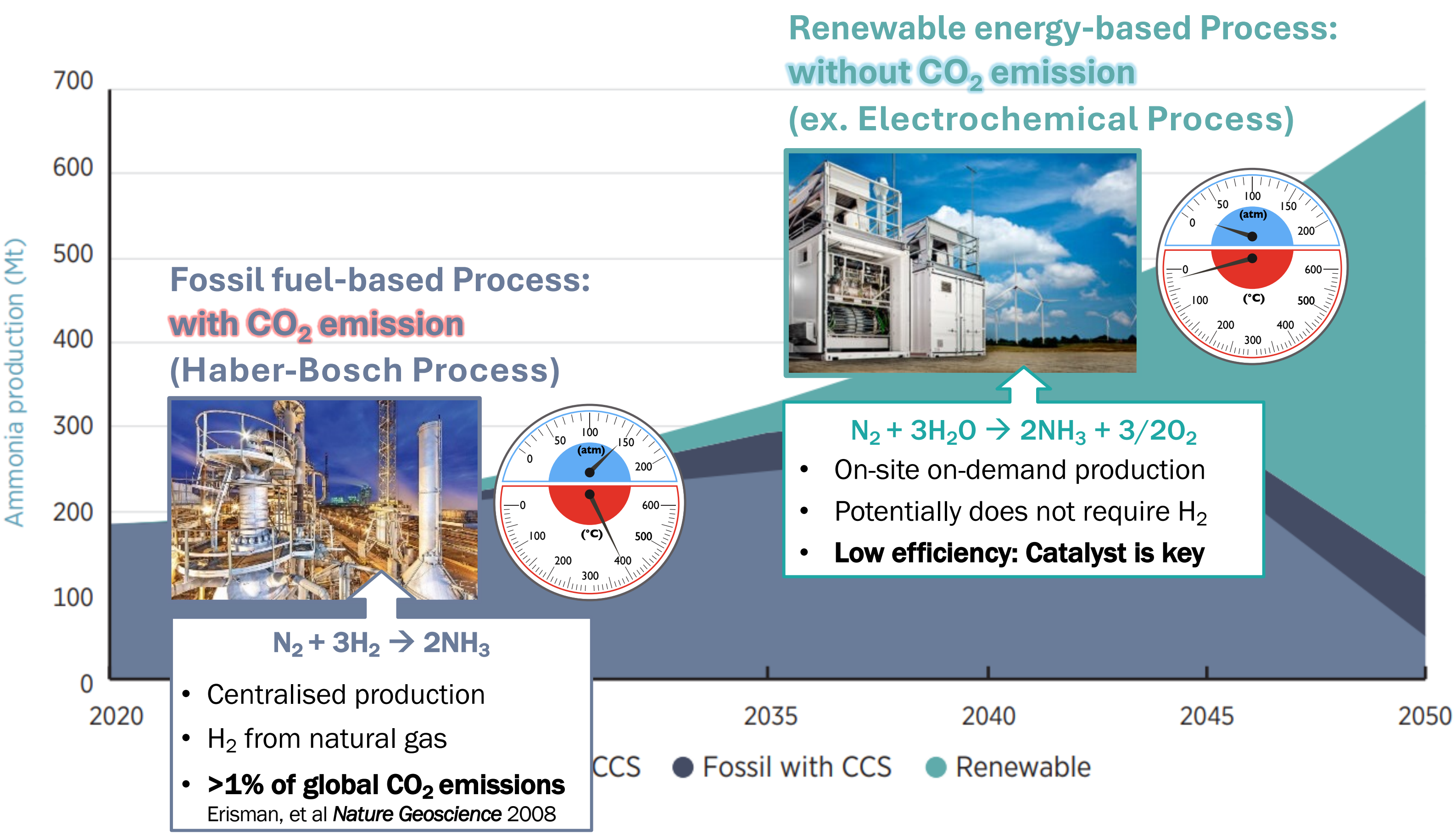
From Fertilizer and Chemicals to Future Sustainable Fuel



Source: Innovation Outlook: Renewable Ammonia — University of Twente Research Information (utwente.nl), Hydrogen Sulfide Fertilizer Spray - Free photo on Pixabay, TradeWinds (tradewindsnews.com), Haber-Bosch process – nh3 fuels, Hydrogen Central (hydrogen-central.com), Missing link for solar hydrogen is… ammonia? (phys.org)

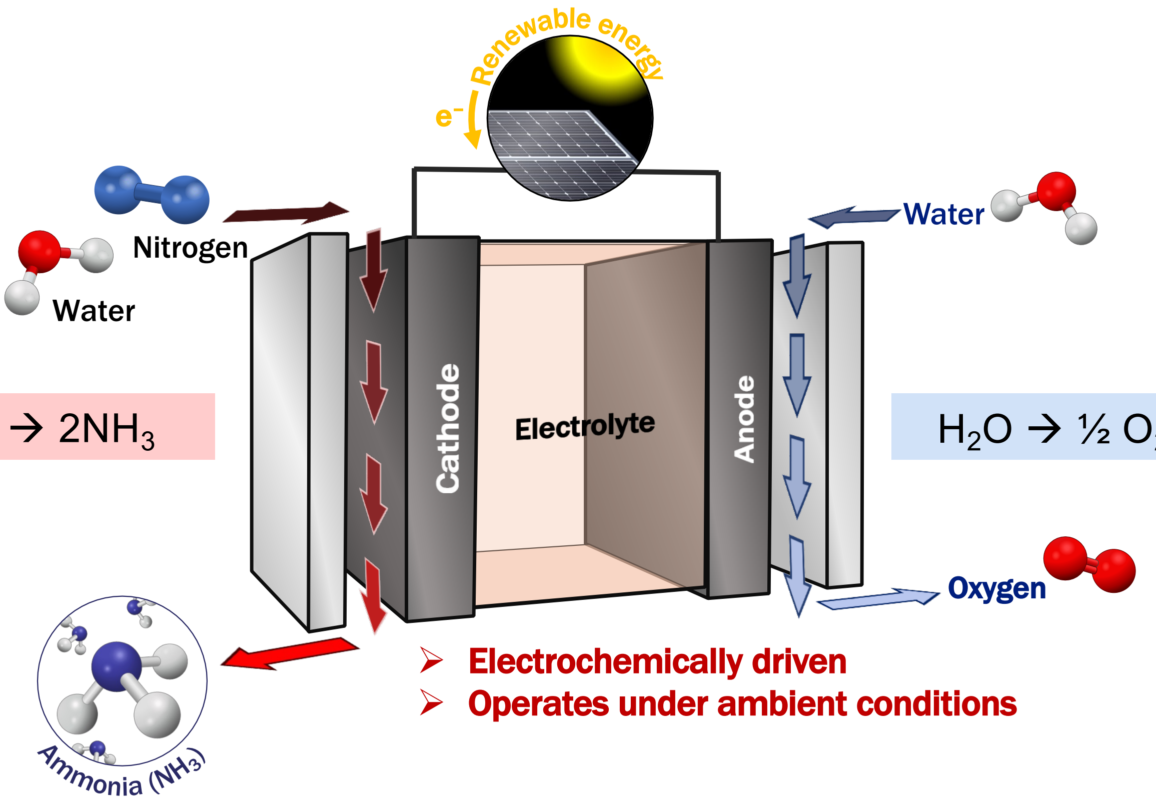
How Do We Make Ammonia?

Harber-Bosch Process is highly optimized but requires significant energy overall



Electrochemical Ammonia Synthesis

Utilizing intermittent renewable energy sources to produce Ammonia



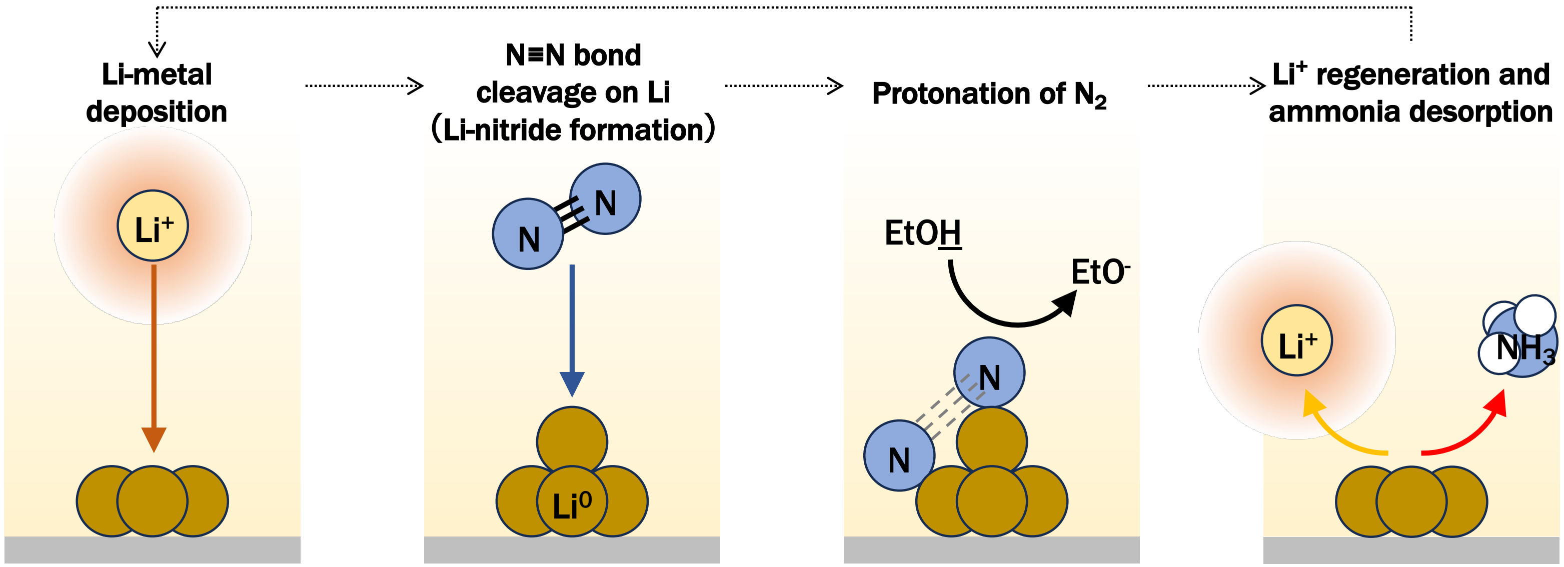
$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$

$H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^-$

- **Electrochemically driven**
- **Operates under ambient conditions**

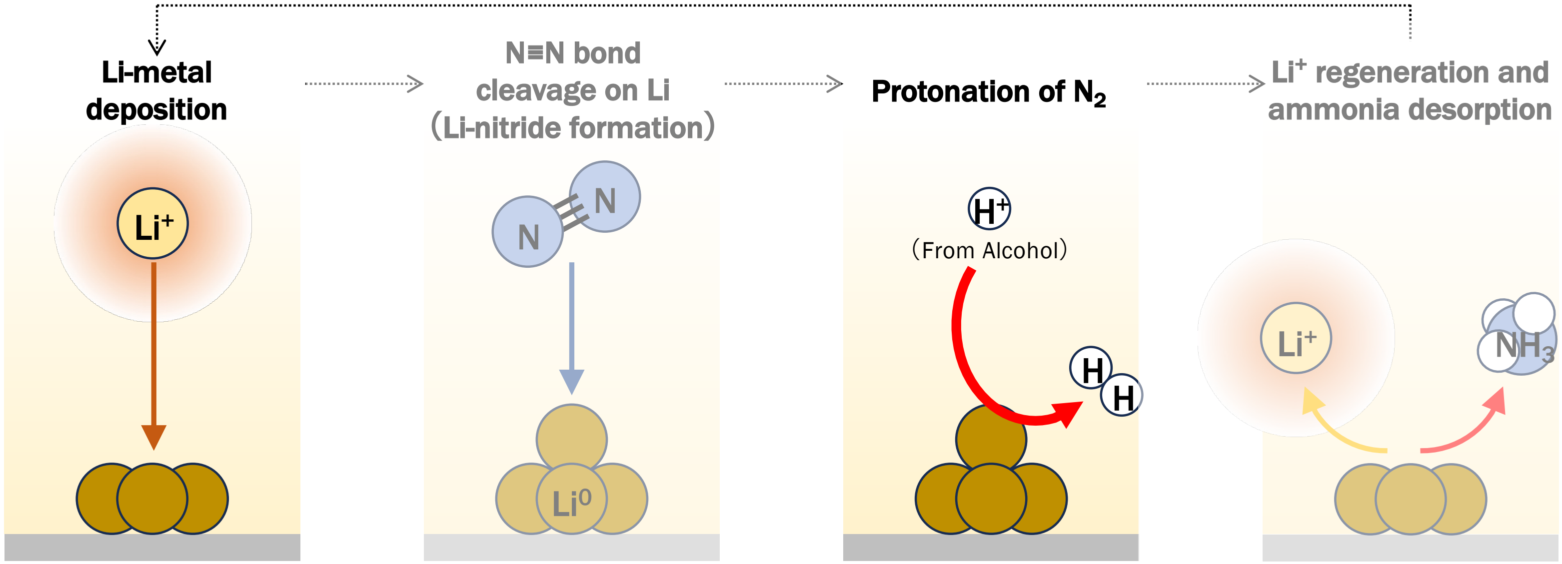
✓ **Simple and scalable system**
✓ **Enables intermittent operation**

Li-mediated Electrochemical Ammonia Synthesis Pathway



- The reaction occurs at the *in situ* deposited Li metal surface
- Typically operates under an organic electrolyte
- Use hydrogen (proton) from alcohol

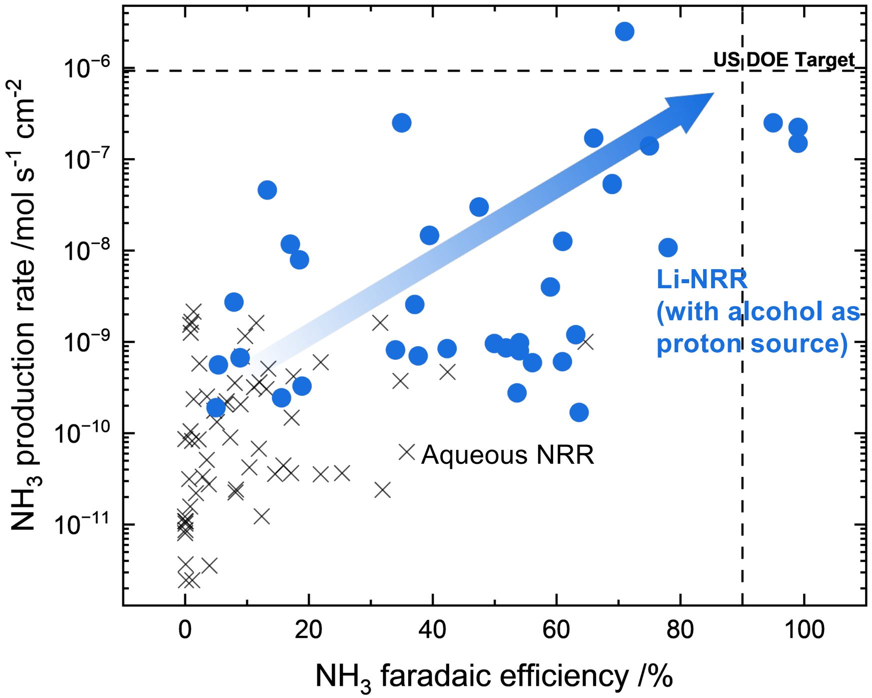
Li-mediated Electrochemical Ammonia Synthesis Pathway



Major Challenge

- Dead Li (=unreacted Li) formation
- Competitive side reaction (H_2 generation, electrolyte decomposition etc.)
- Consumption of alcohol during the operation

Significant Improvement in Past ~10 Years



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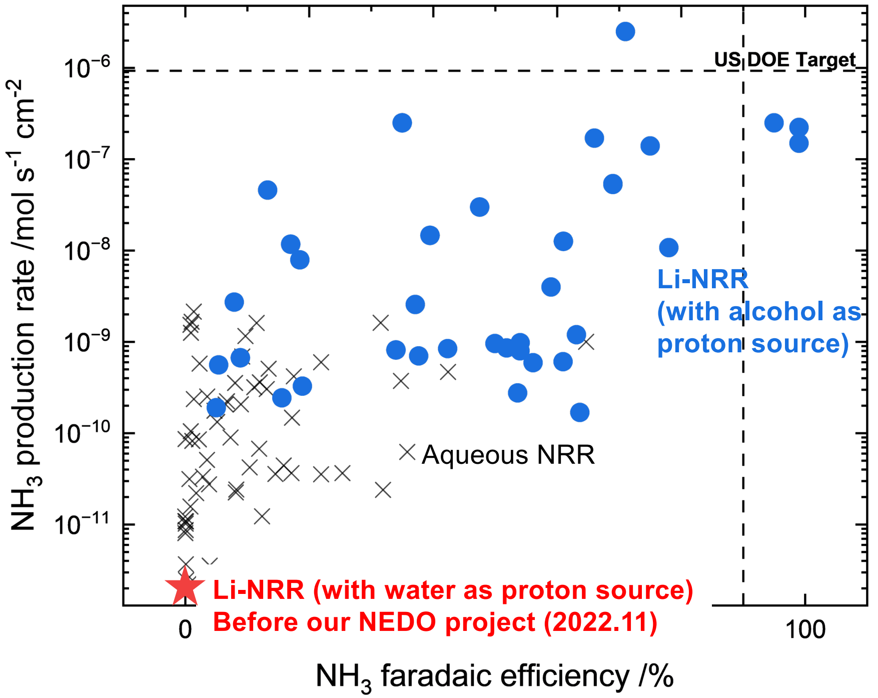


But not for Li-NRR using water as a proton source

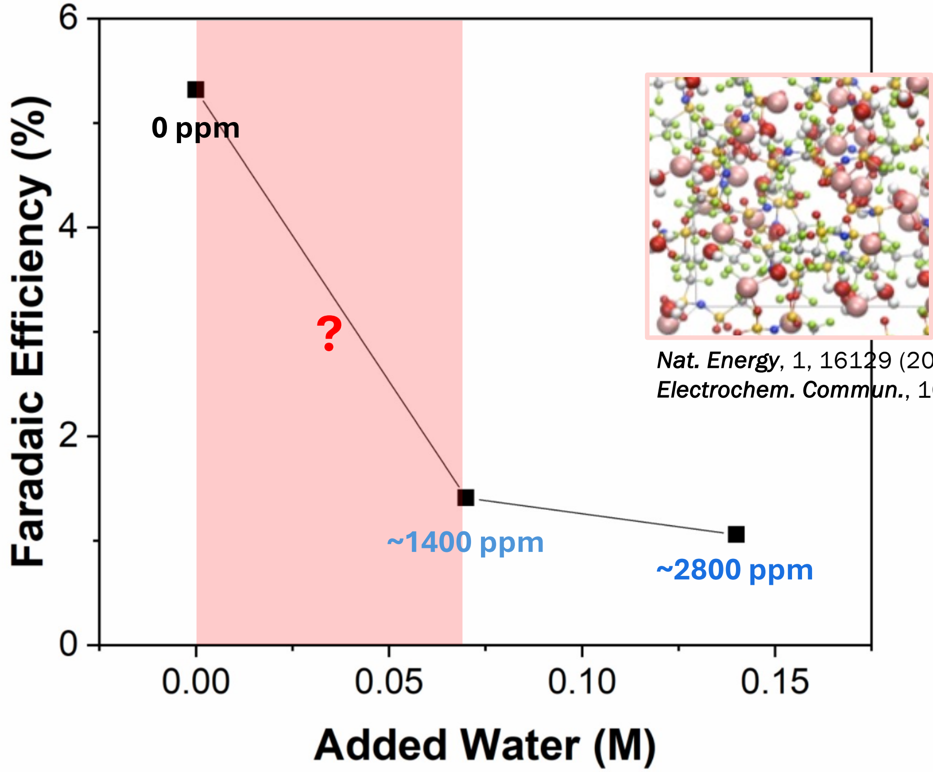
Major Challenge

- Dead Li (=unreacted Li) formation
- Competitive side reaction (H_2 generation, electrolyte decomposition etc.)
- Consumption of alcohol during the operation

Ideal Proton Source: Water

What happens if we replace alcohol with water?

→ FE drops significantly due to the competitive water reduction reaction

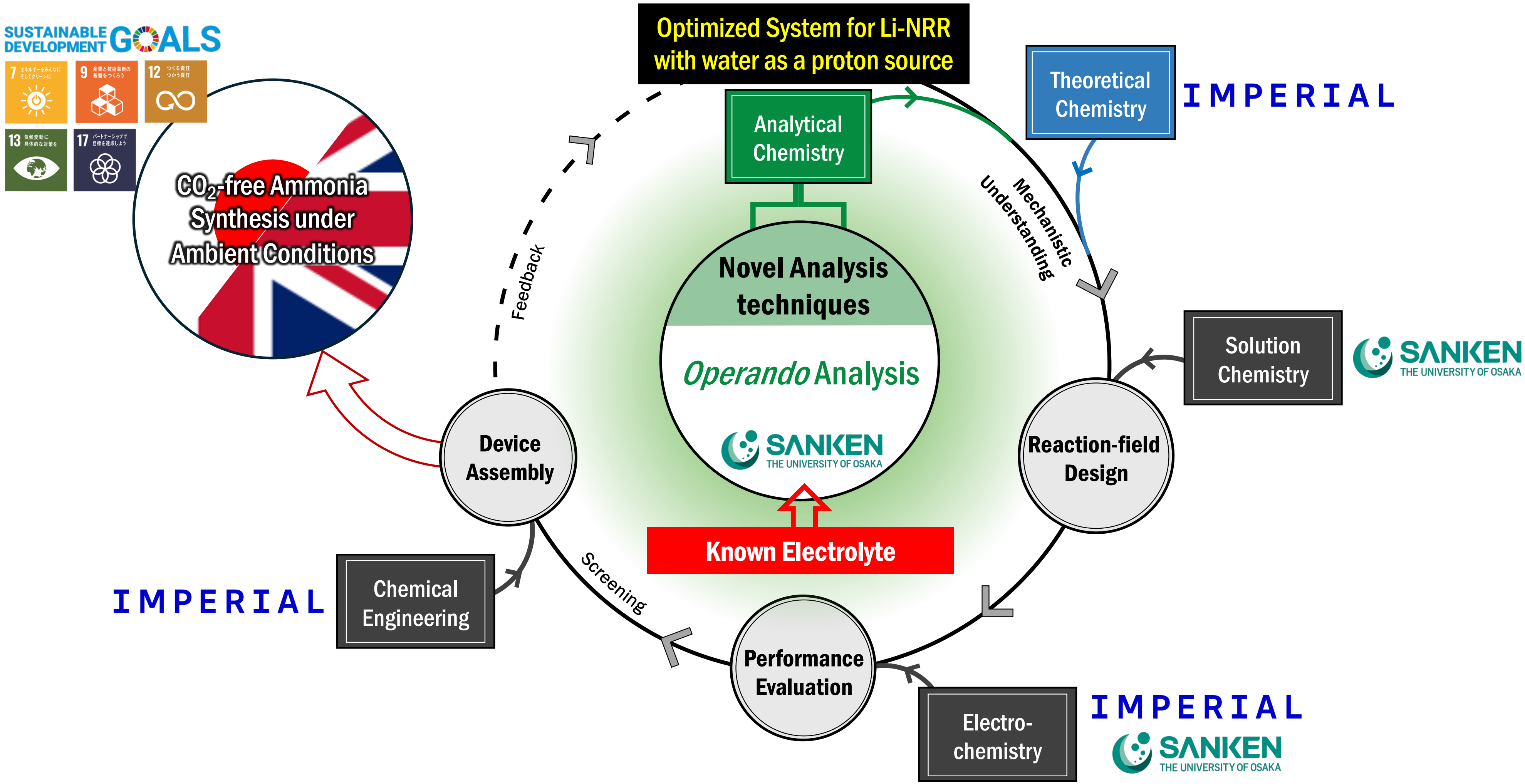


"Isolated" water makes water more stable

Nat. Energy, 1, 16129 (2016); *Angew. Chem. Int. Ed.*, 58, 14202 (2019); *Electrochem. Commun.*, 104, 106488 (2019)

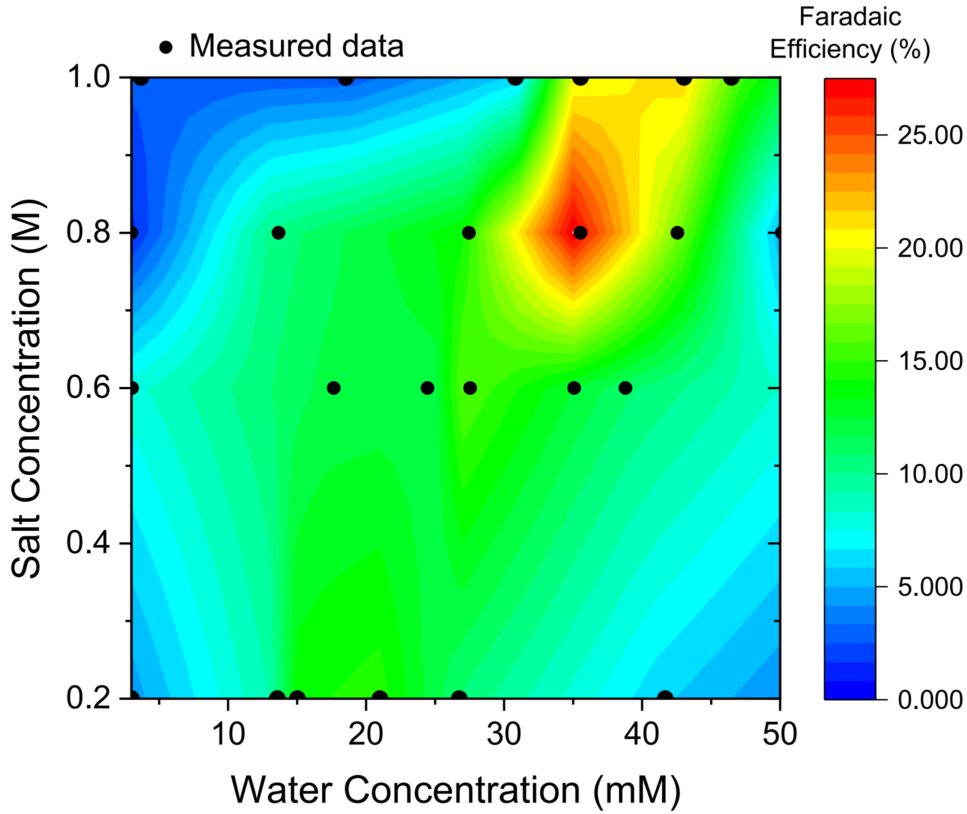
Lazouski, N., et al. Joule 3, 1127–1139 (2019).

NEDO International Collaboration Scheme: Team up with Imperial



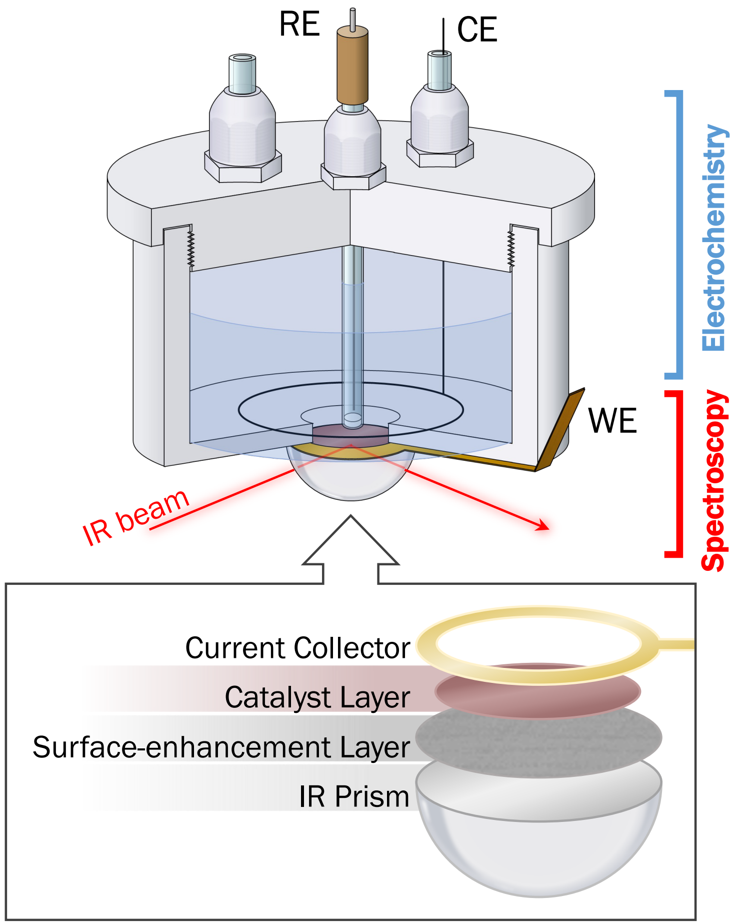
Electrolyte Engineering Enables Use of Water as a Proton Source

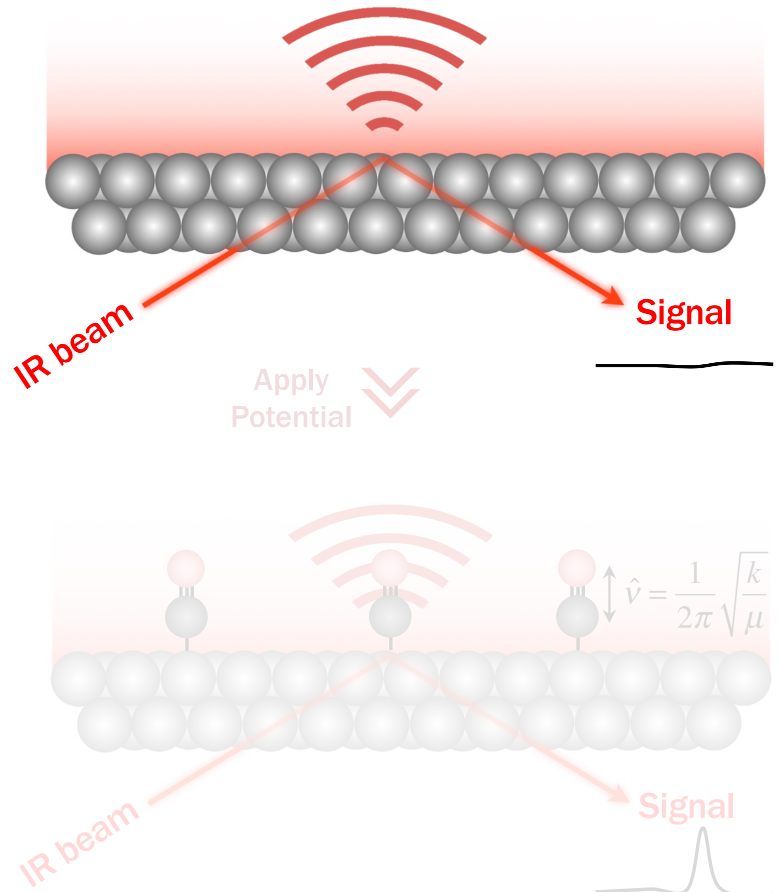
Precise tuning of salt and water concentration reveals the "hotspot" for ammonia synthesis



What is Happening at the Electrode-Electrolyte Interface?

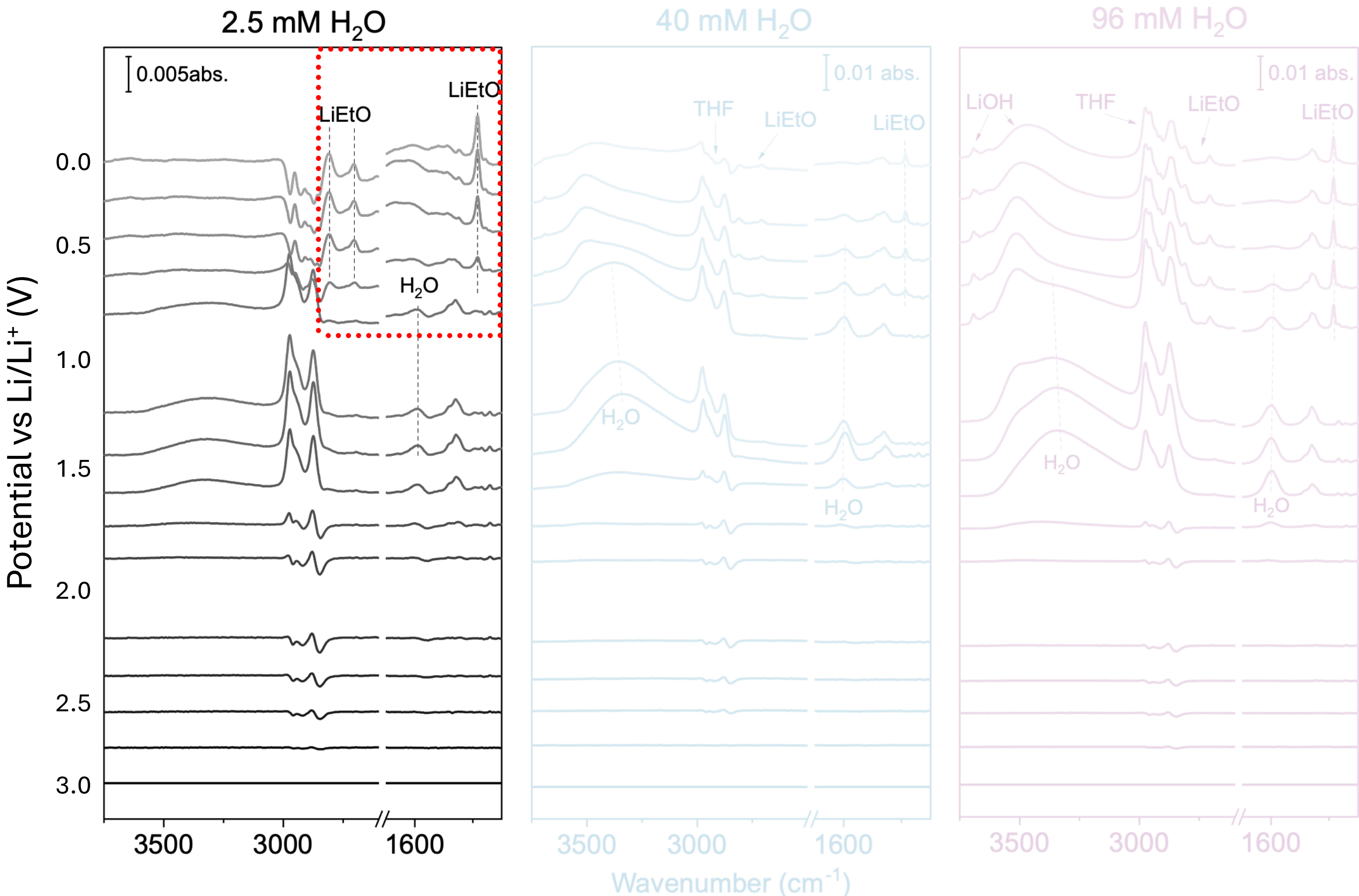
Real-time observation with *operando* SEIRA spectroscopy

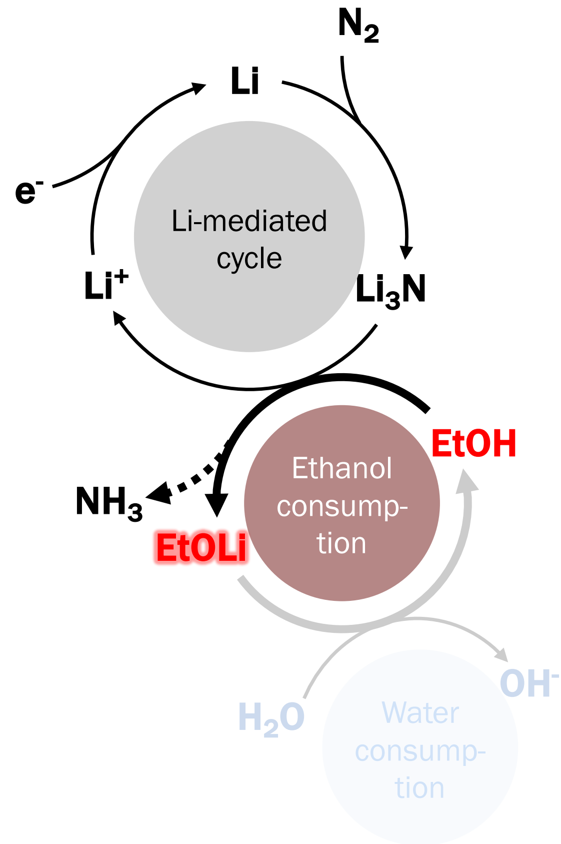




What is Happening at the Electrode-Electrolyte Interface?

Under dry conditions, EtOLi (the reacted form of ethanol) is accumulated on the surface





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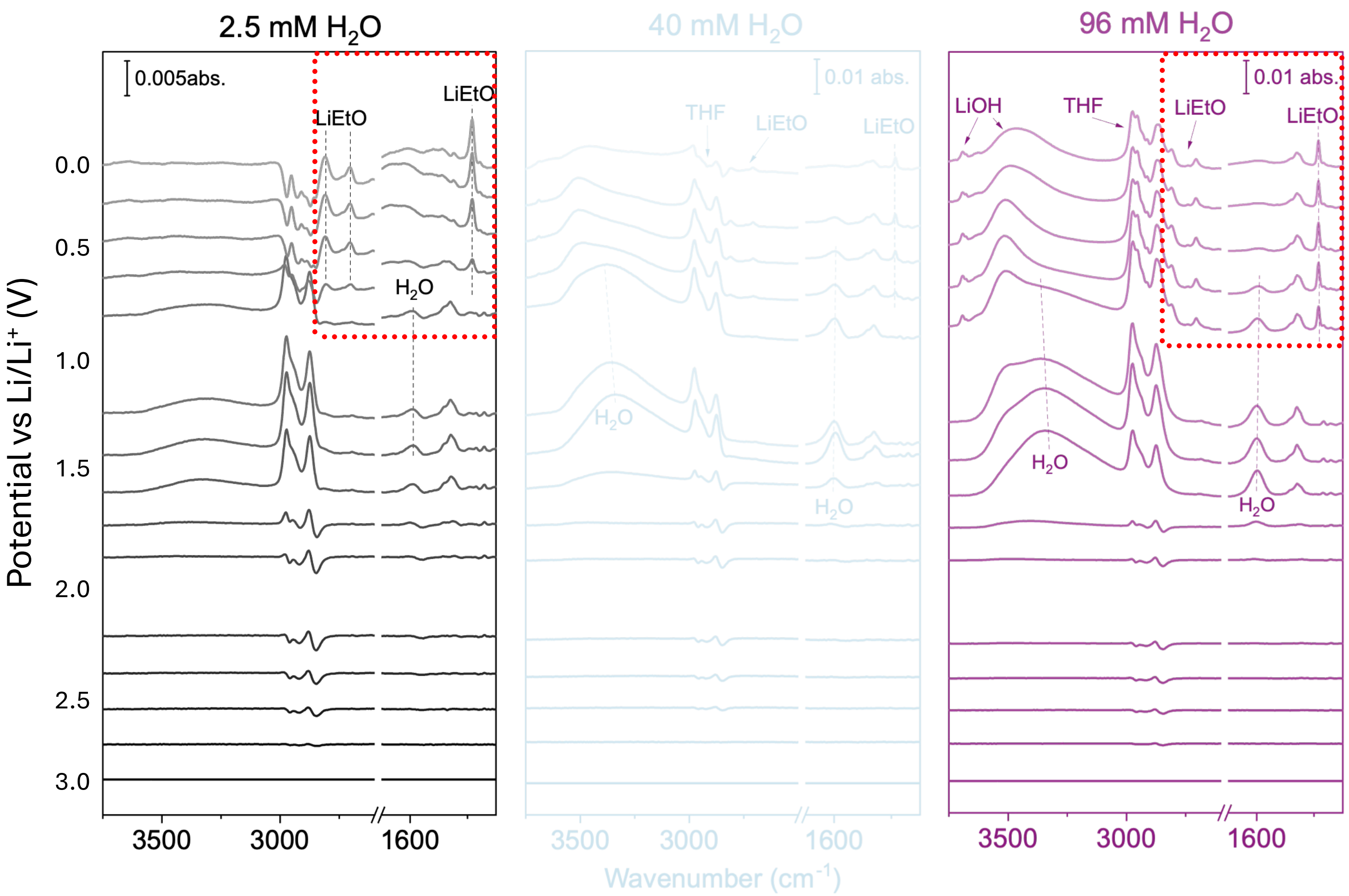
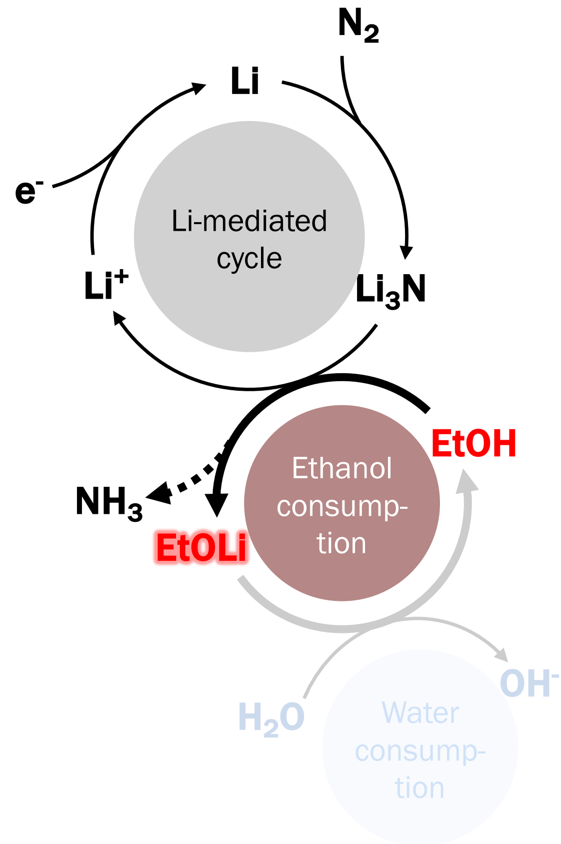
What is Happening at the Electrode-Electrolyte Interface?

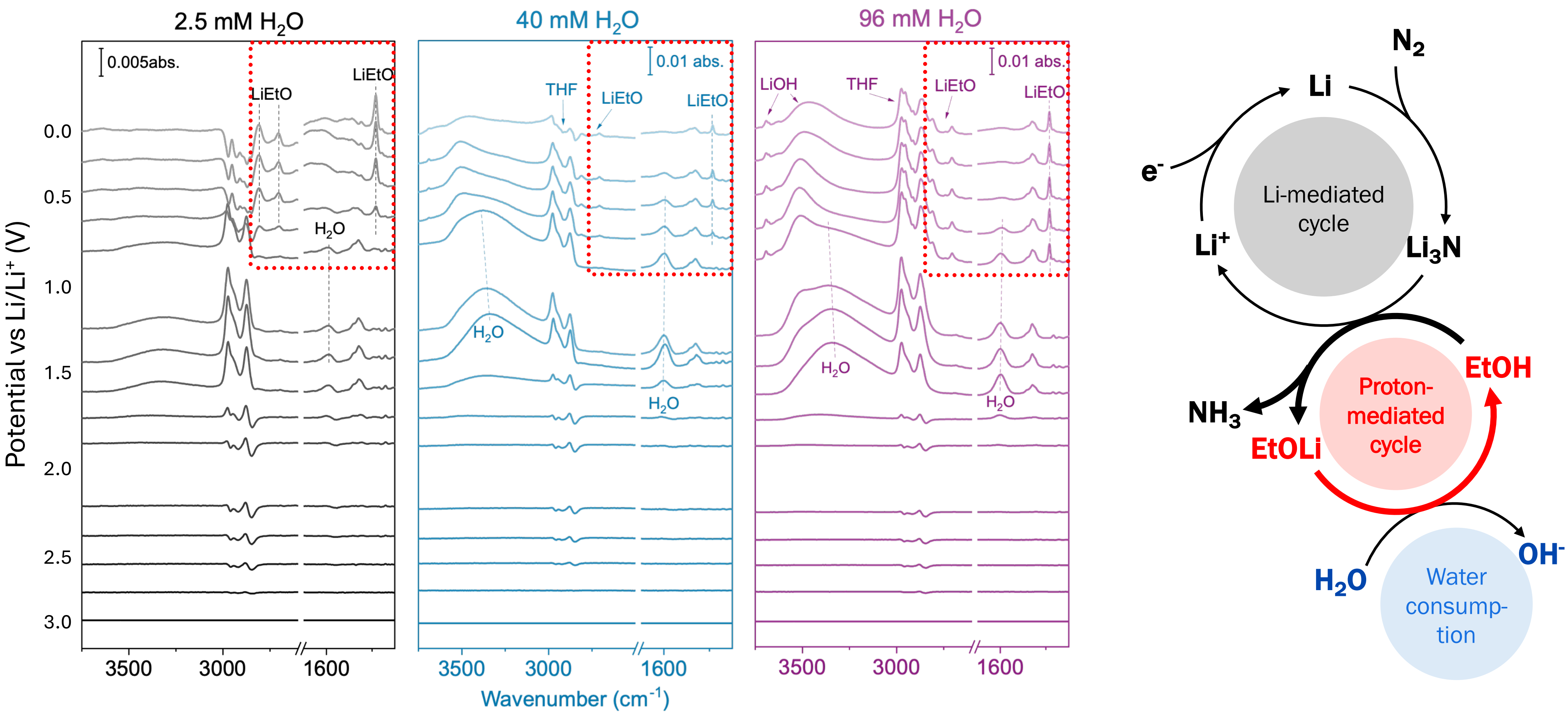
Under excess water conditions, EtOLi is also accumulated on the surface





What is Happening at the Electrode-Electrolyte Interface?

The optimal amount of water can drive the proton-mediated cycle and regenerates ethanol



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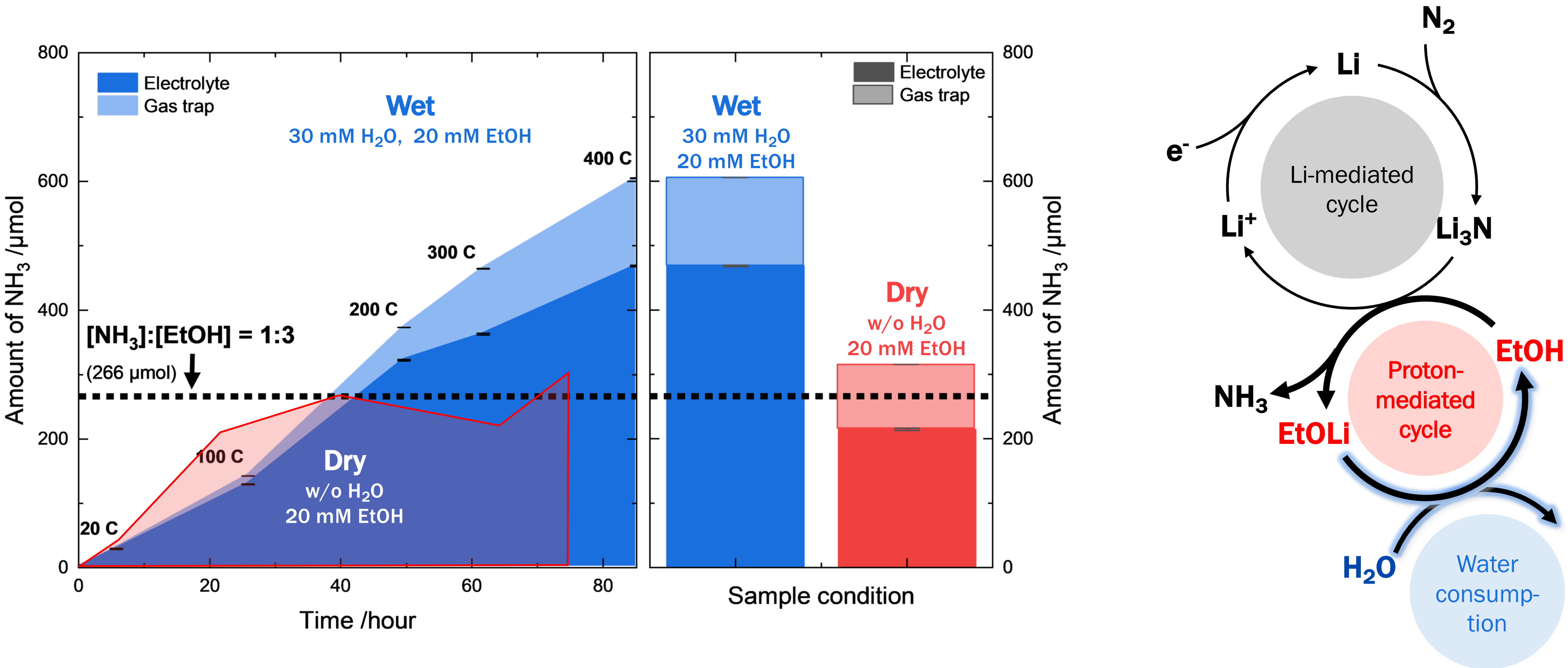
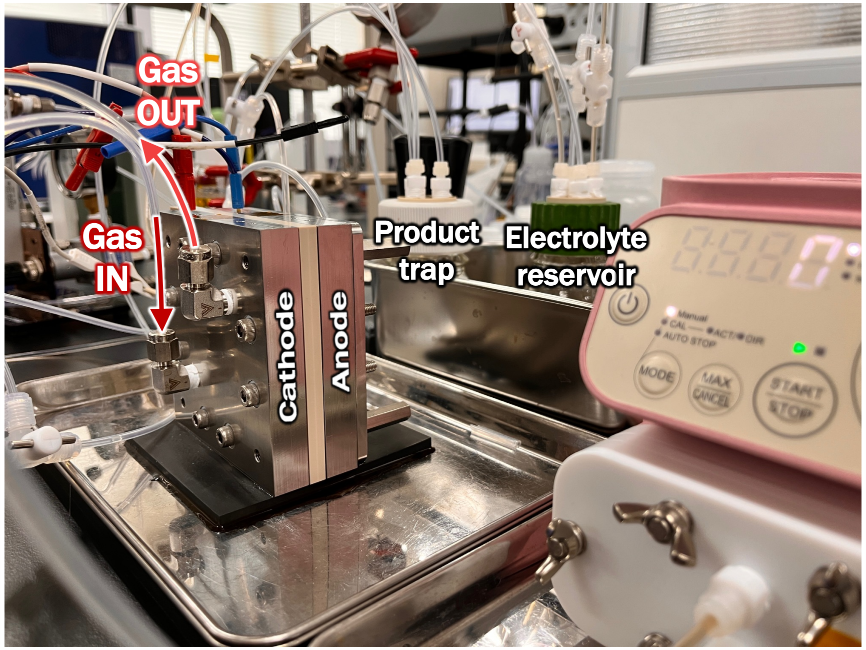
"Indirect" Water Utilization Enables Ethanol Regeneration

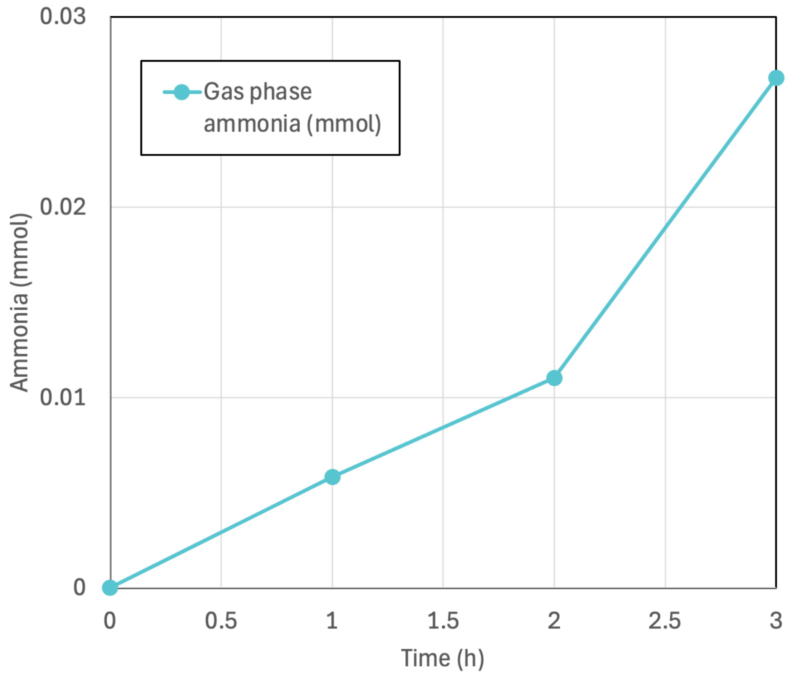
Water regenerate ethanol and enable continuous ammonia production without consuming ethanol



Performance of the Prototype Ammonia Synthesis Cell

Ammonia is produced continuously at a production rate of 7.2×10^{-9} mol sec^{-1} cm^{-2}





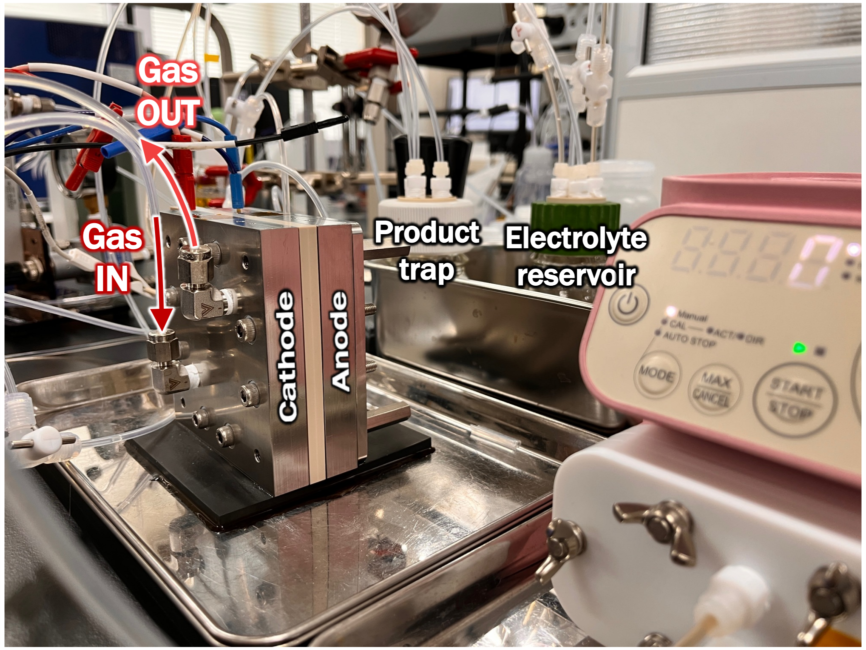
Developed Gas-Diffusion type Full Cell

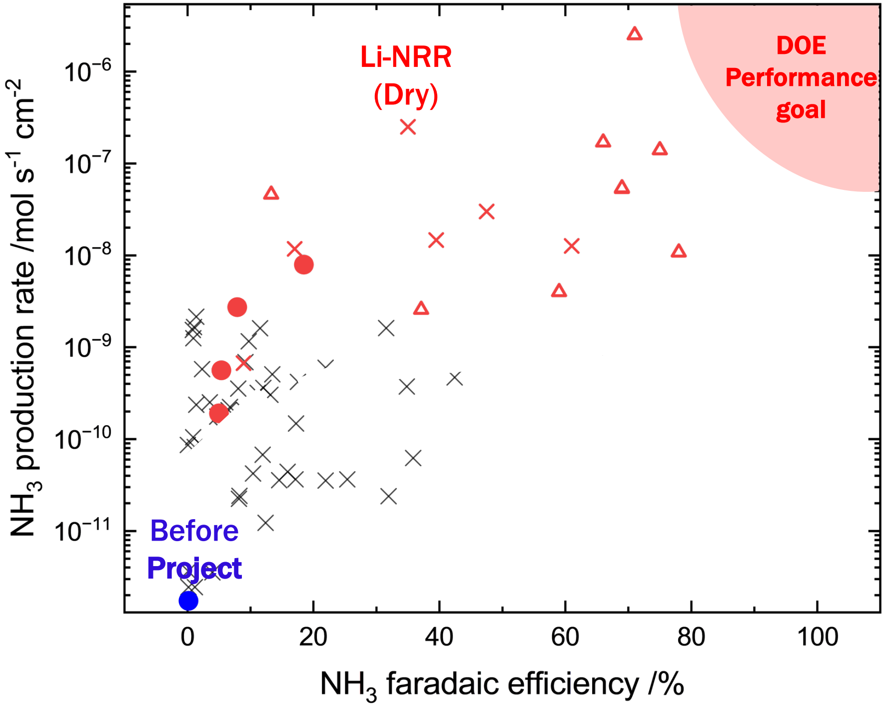
➢ **Current Efficiency**	**>60% (with water as "indirect" proton source)***
➢ Potential Efficiency	~32%
➢ Ammonia Production Rate	7.2×10^{-9} mol sec^{-1} cm^{-2}

* The world's highest value based on our literature search

Performance of the Prototype Ammonia Synthesis Cell

Highest current efficiency achieved for the Ammonia synthesis using water





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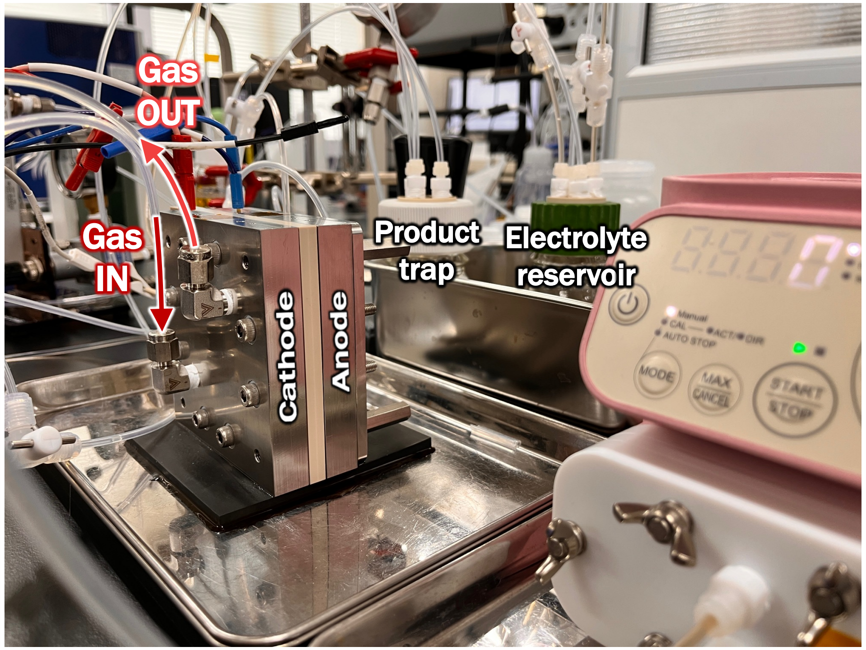

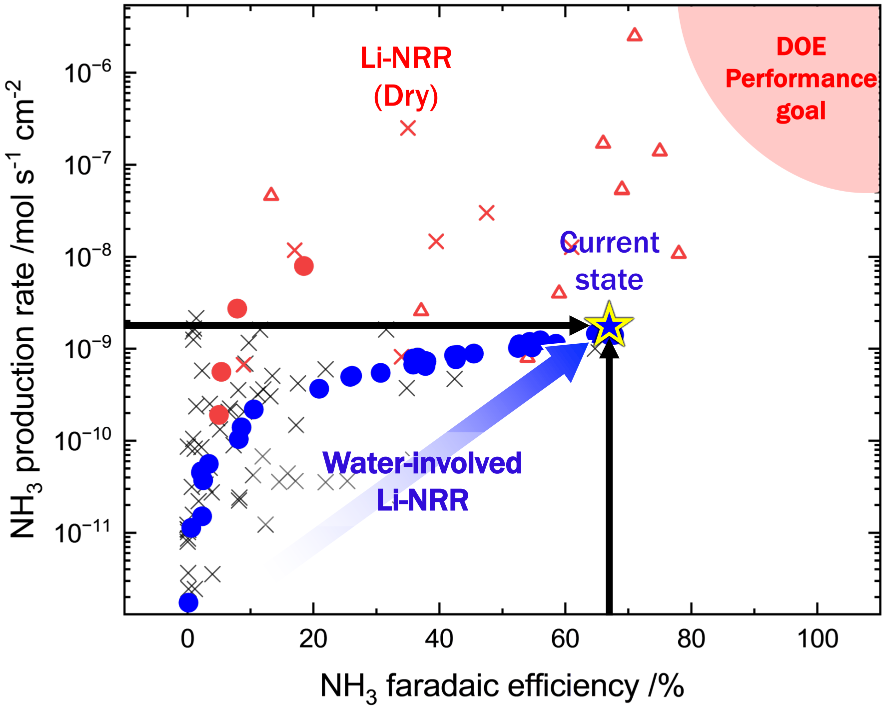

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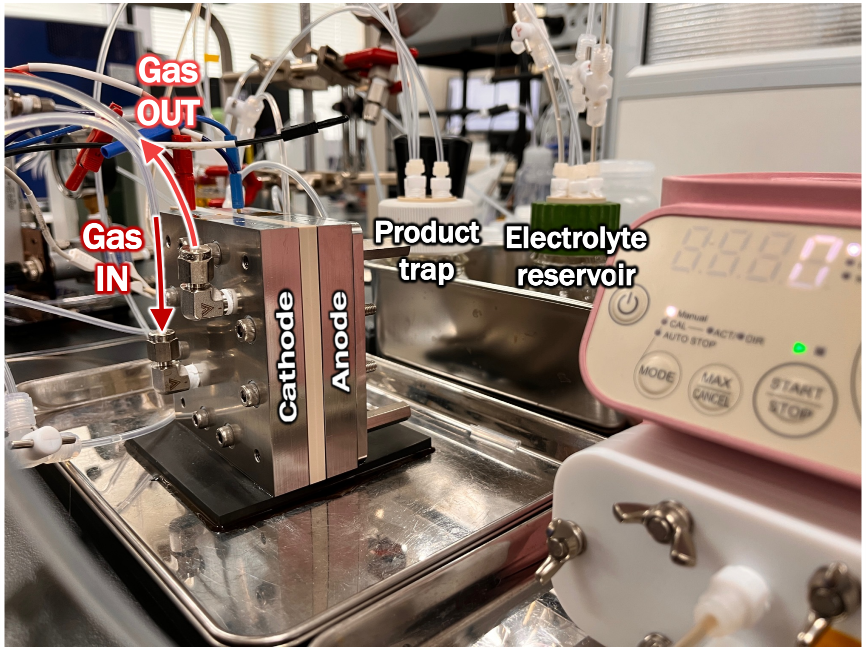
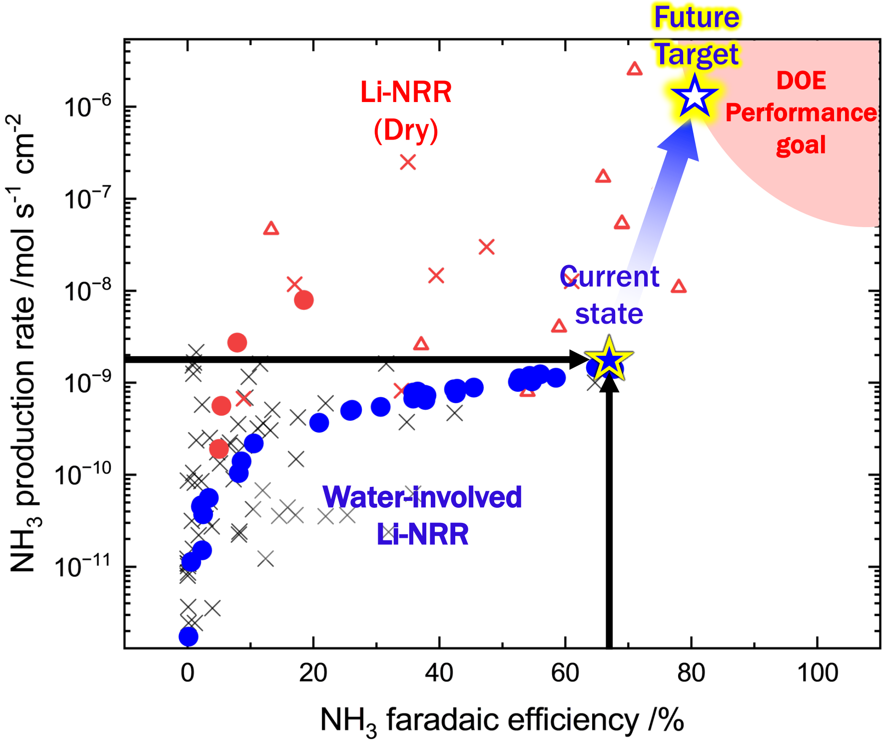
Performance of the Prototype Ammonia Synthesis Cell

Next Goal: Increase the ammonia production rate while improving the efficiency





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Towards Decentralized, Resilient, Sustainable Ammonia Production

International collaboration accelerates the R&D for sustainable ammonia synthesis

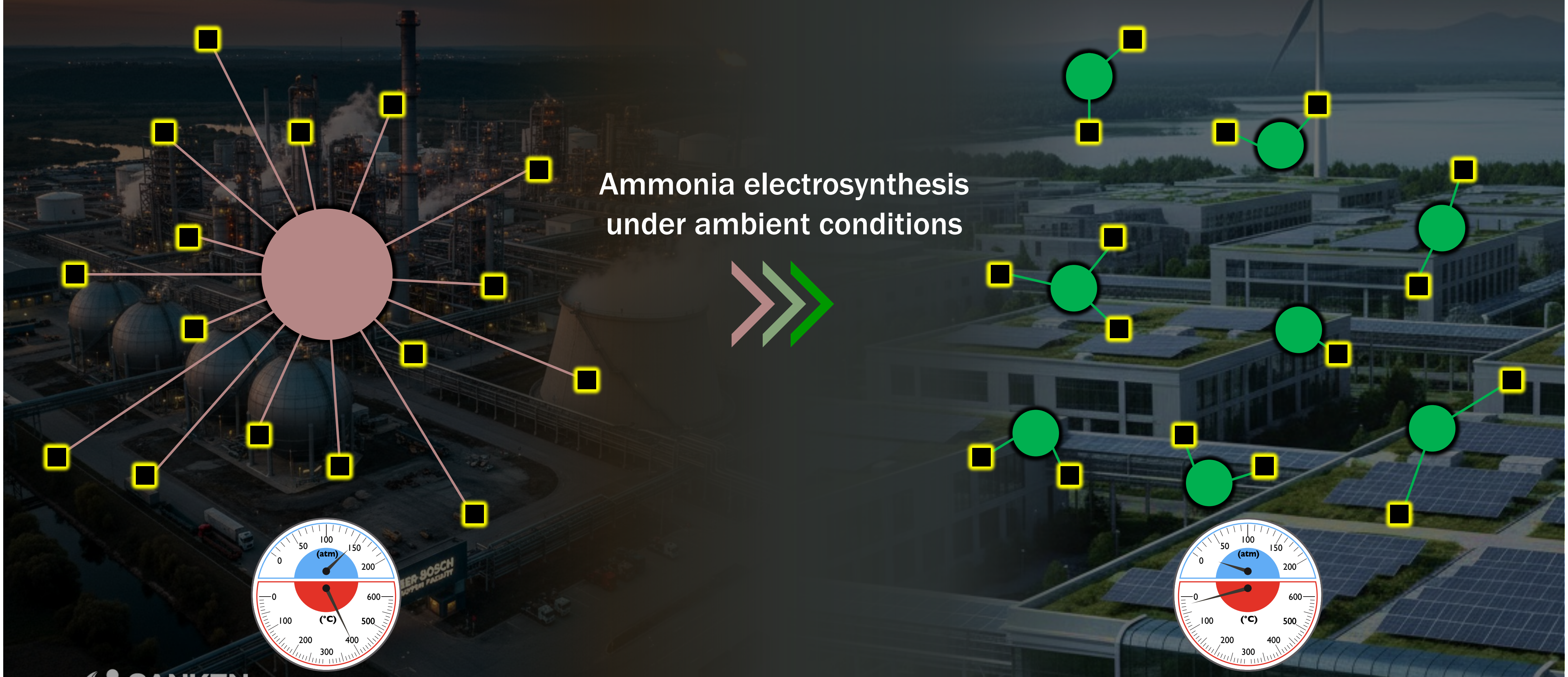

Image created by Gemini AI

Acknowledgements

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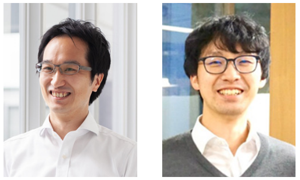
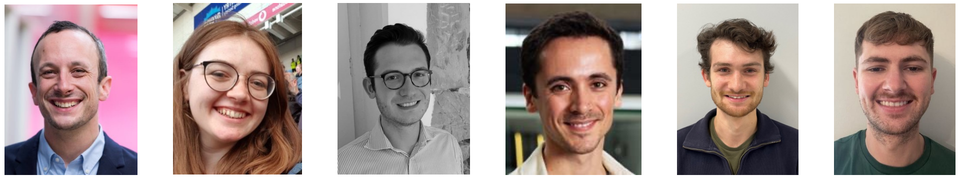


IMPERIAL



NEDO

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