Materials and Systems Engineering Lab (MaSEL)

NETL Ammonia Combustion Technology Group

July 8th, 2025

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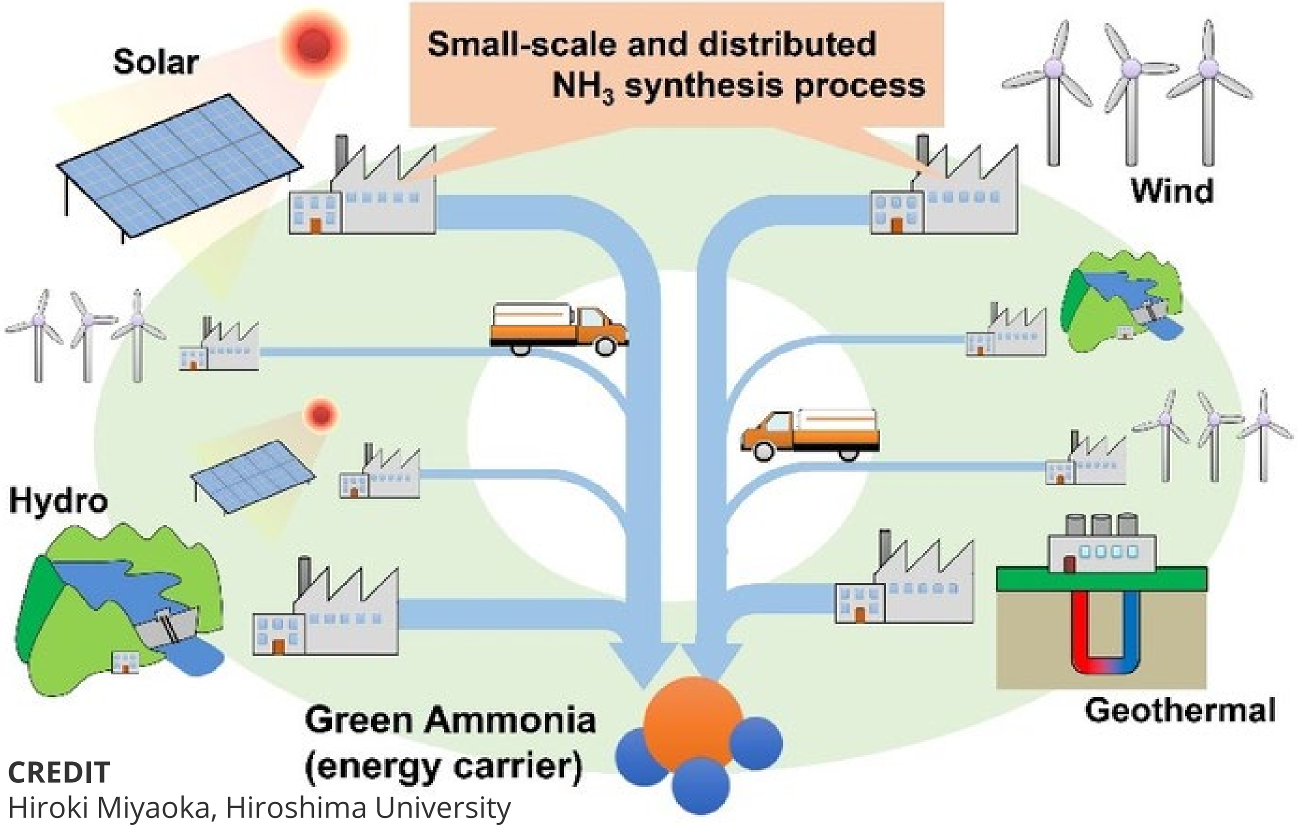

CREDIT
Hiroki Miyaoka, Hiroshima University

METAL NITRIDE MEDIATED AMMONIA SYNTHESIS

Prof. Meenesh R Singh
Professor of Chemical Engineering,
University of Illinois Chicago

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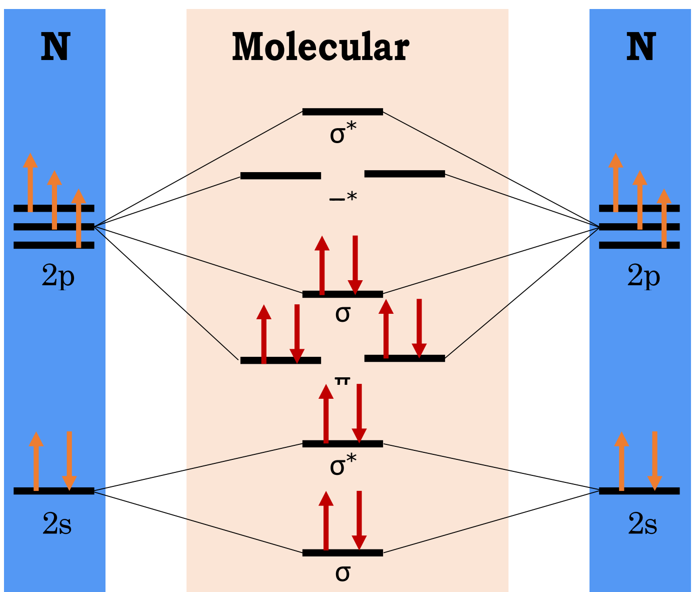
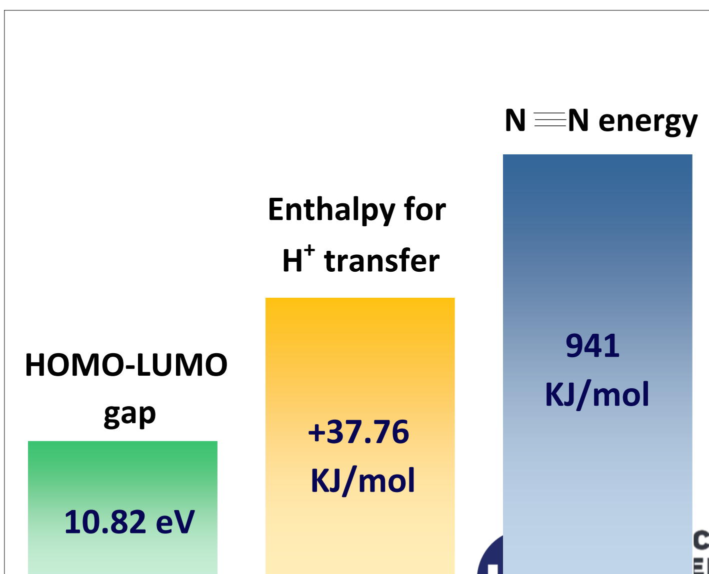
Comprehending the MOT for N_2 to NH_3

N_2 Bonding and Molecular orbitals

- The triple bond inN_2 consists of one sigma and two pi bonds
- The sigma bond is formed by head on overlap while pi bonds result from lateral overlap of atomic orbitals
- HOMO is in the sigma bond and LOMO is pi antibonding orbitals

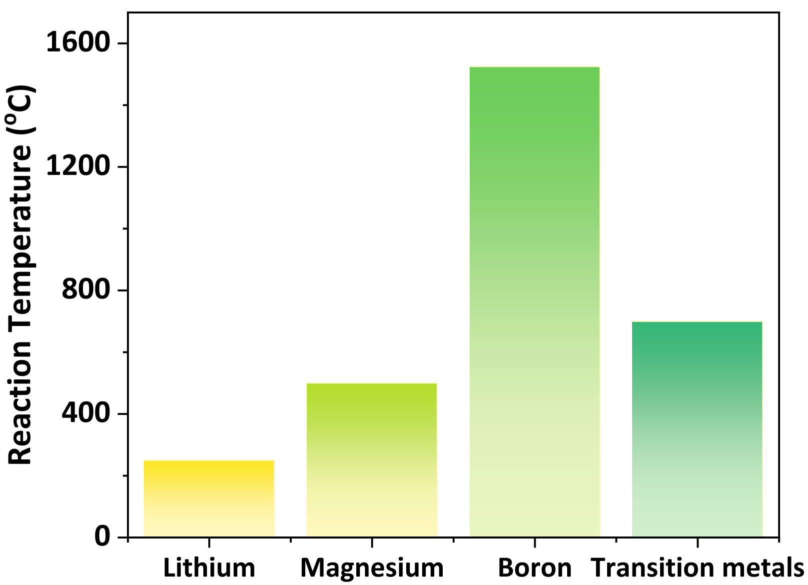


Why N_2 activation is a challenge?



Reactivity of Metal Nitrides

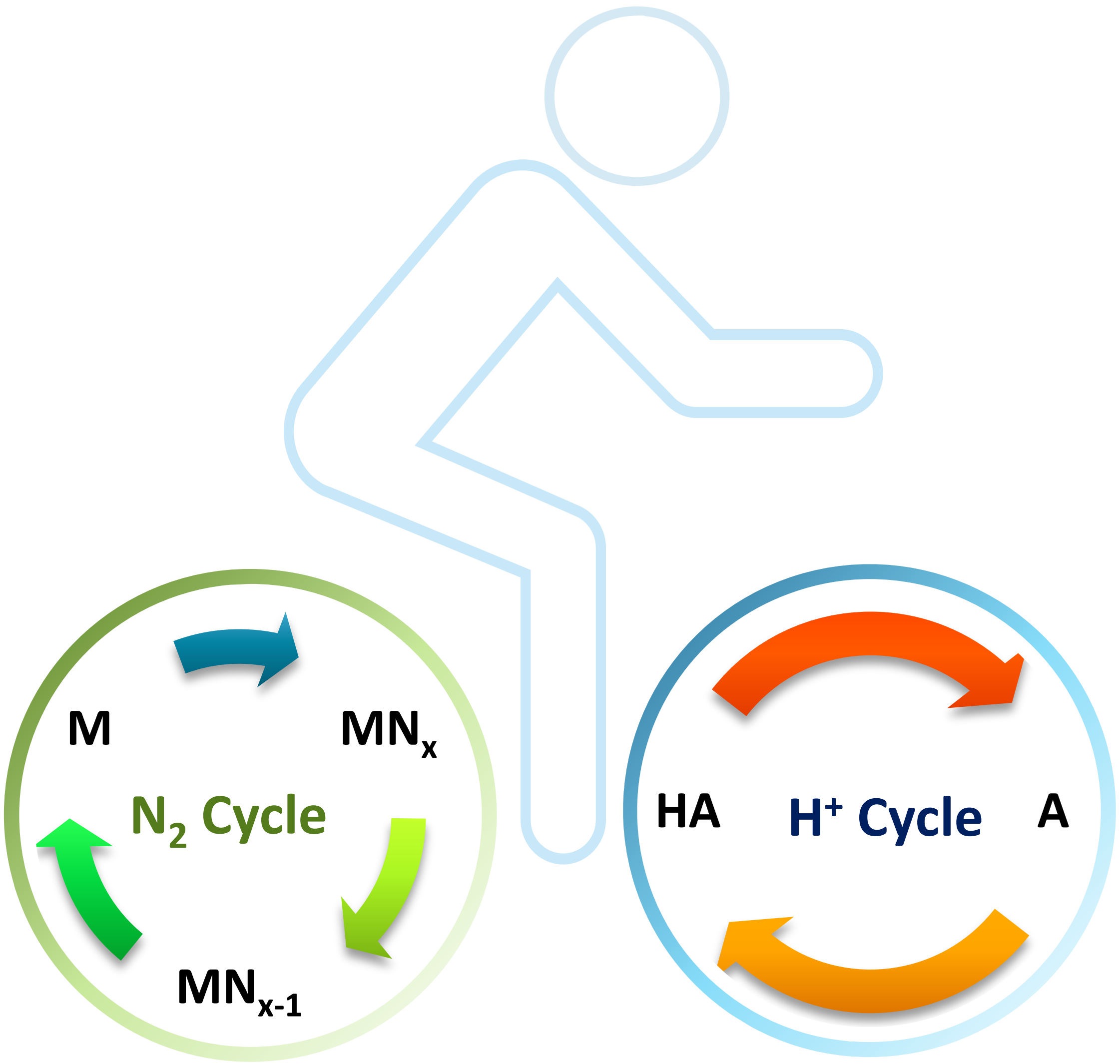
- N_2 is largely inert at room temperature (~25°C). However, it reacts with certain metals at elevated temperatures.
- The reactivity varies: Li reacts with N_2 at 250°C, while alkaline earth metals like Mg react rapidly at temperatures above 500°C.
- At high temperatures, N_2 reacts with metals like Li, Mg, B, Al and transition metals to form nitrides



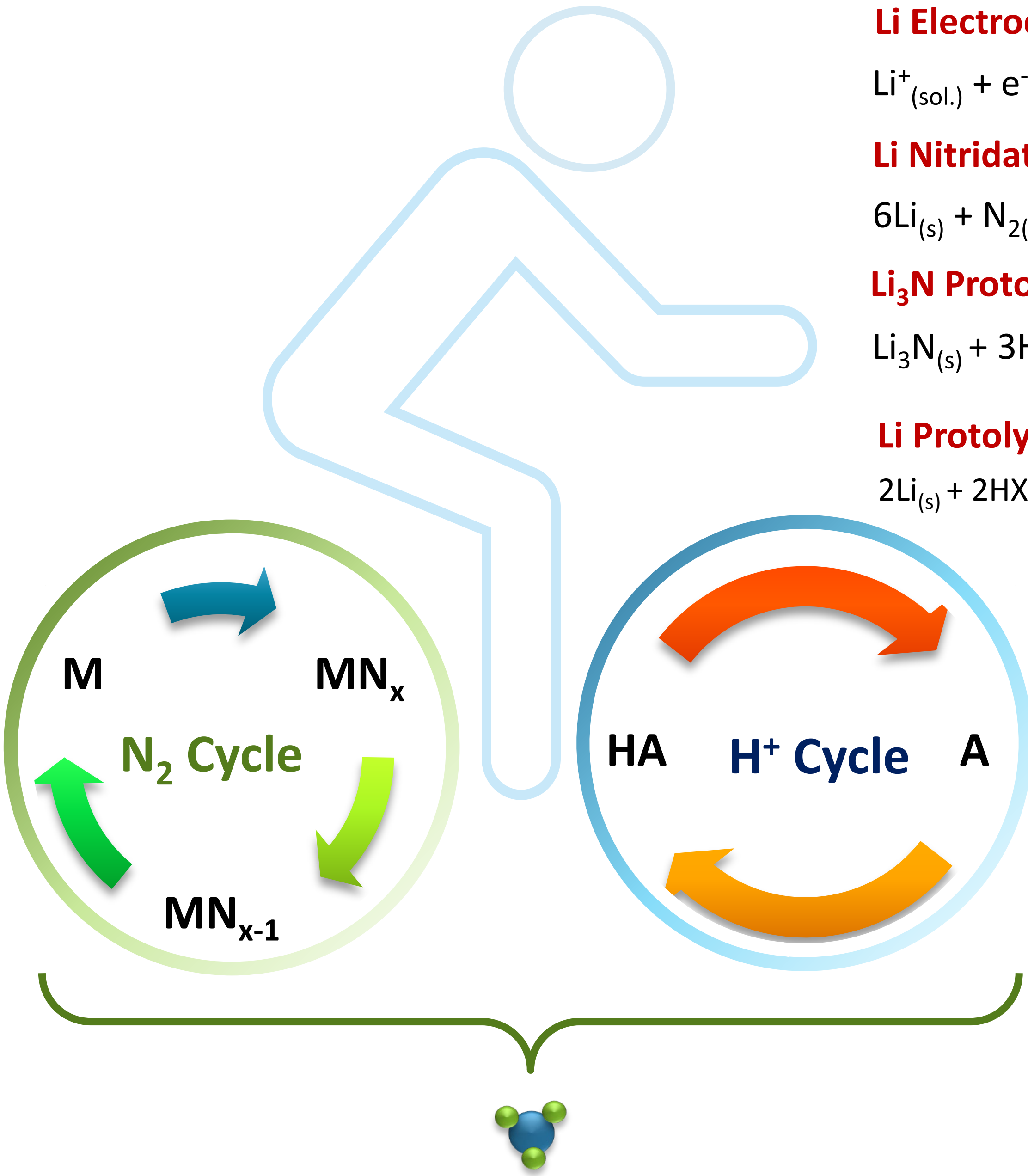
Types of Nitrides

- Ionic – Li_3N, Mg_3N_2
- Covalent – BN, Si_3N_4, P_3N_5
- Interstitial – W_2N, TiN

Implementing Mediated NH_3 Synthesis



Implementing Mediated NH_3 Synthesis



Li Electrodeposition

$$Li^+_{(sol.)} + e^- \longrightarrow Li_{(s)}$$

Li Nitridation

$$6Li_{(s)} + N_{2(sol.)} \longrightarrow 2Li_3N_{(s)}$$

Li_3N Protolysis

$$Li_3N_{(s)} + 3HX_{(sol.)} \longrightarrow NH_{3(sol.)} + 3\ Li^+_{(sol.)} + 3X^-_{(sol.)}$$

Li Protolysis

$$2Li_{(s)} + 2HX_{(sol.)} \longrightarrow H_{2(g)} + 2\ Li^+_{(sol.)} + 2X^-_{(sol.)}$$

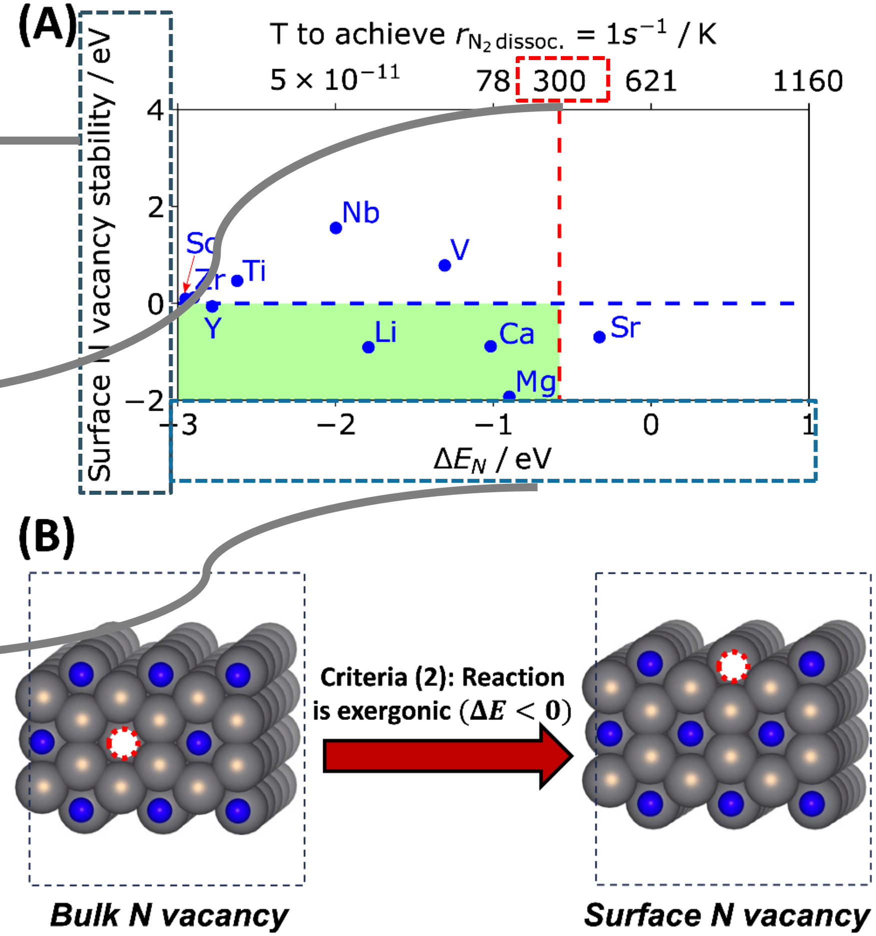
The two cycles must remain in harmony with each other; otherwise, any imbalance will result in limiting behavior

Understanding Theoretical Activity Descriptors for MediatedNH_3 Synthesis

Stability of surface N vacancy in the nitride with respect to the bulk nitride (E_{surf} - E_{bulk})

Spontaneous nitride formation at room temperature

Strong binding of N to the clean metal (deposited metal)

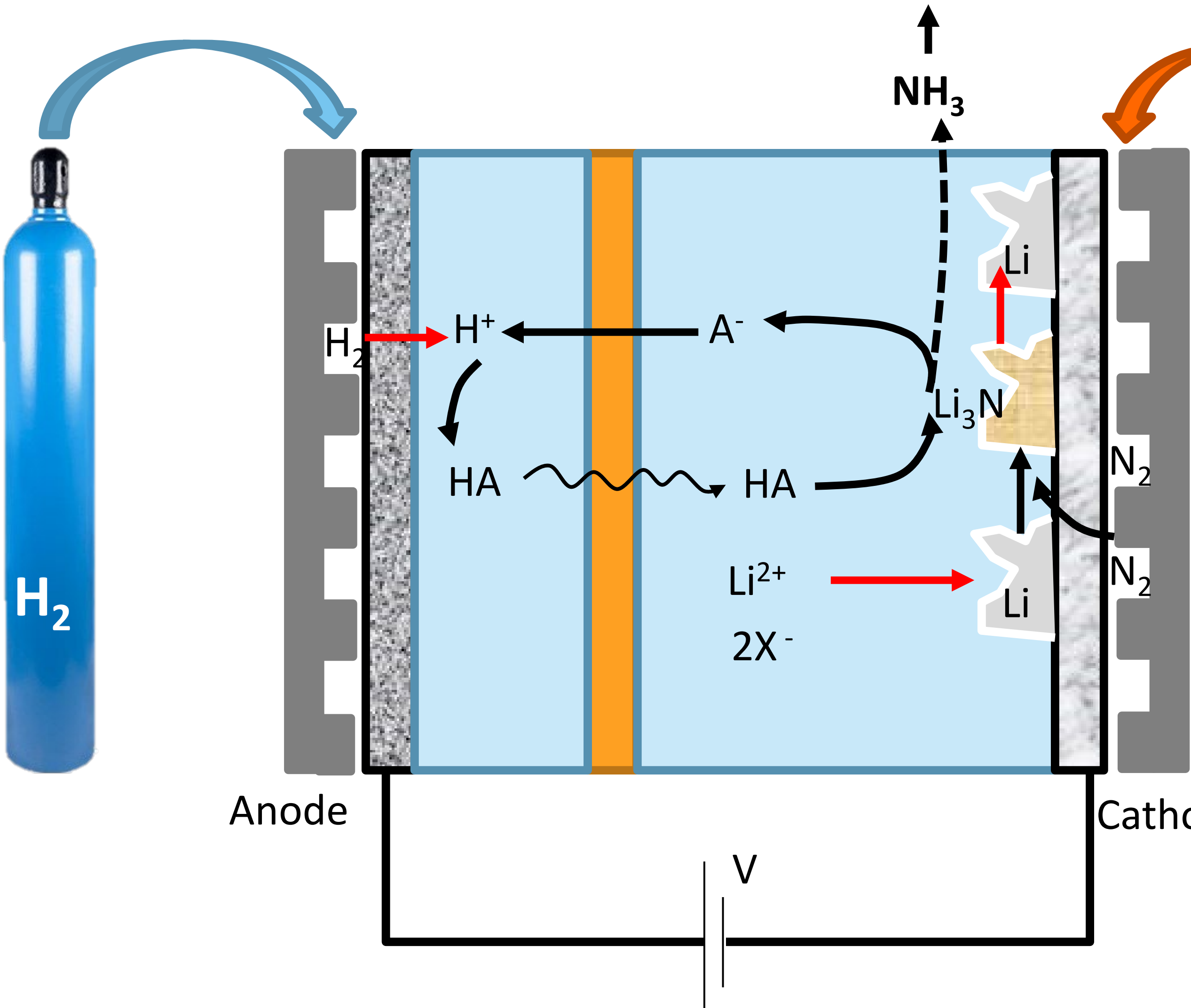


Apart from Li, Ca and Mg also satisfy the criteria to be substitutions for mediated ammonia synthesis

Prof. Gauthier, TTU

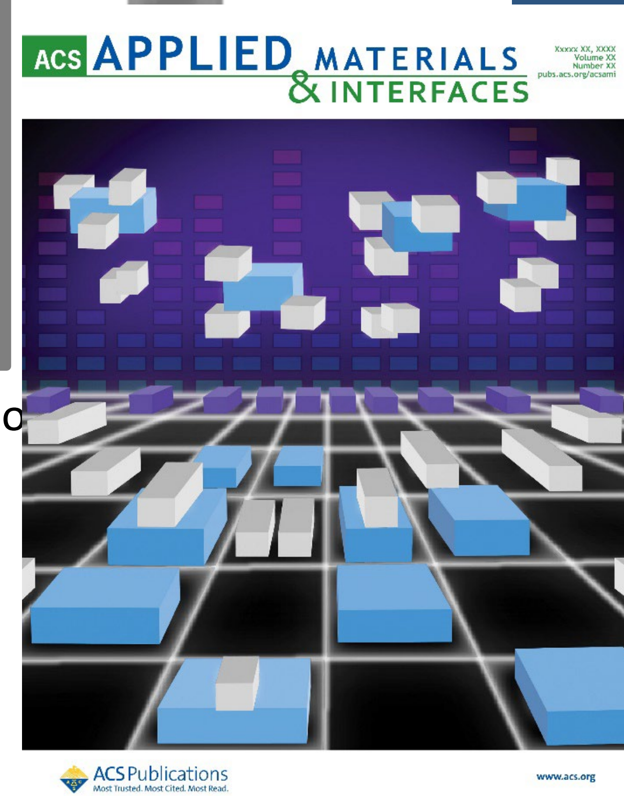
Dr. AR Singh

Li-Mediated Ammonia Synthesis



Lithium-Mediated NH_3 Synthesis

(Patented Technology – UIC)



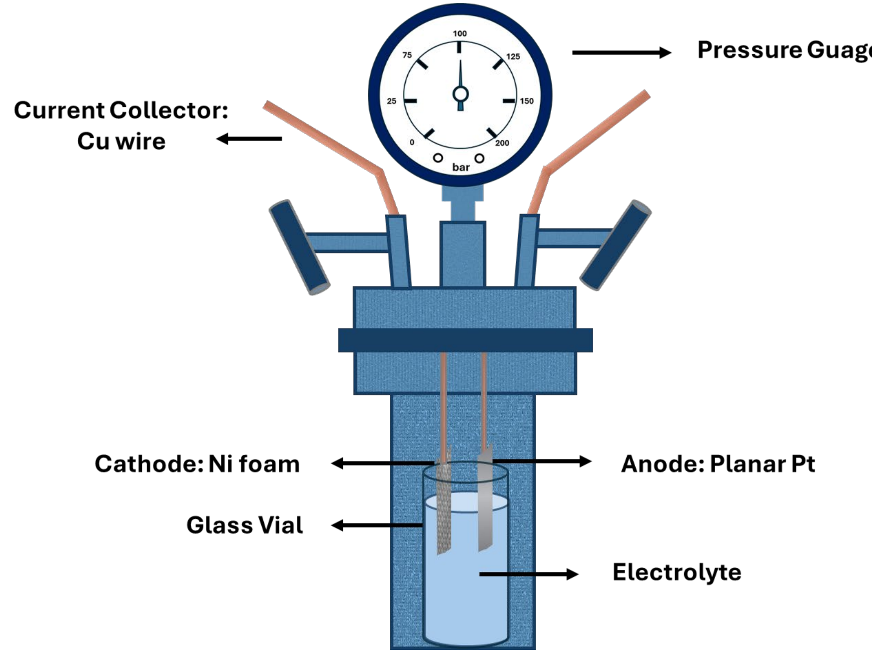
Parameters that Affect Solid-Electrolyte Interface (SEI)

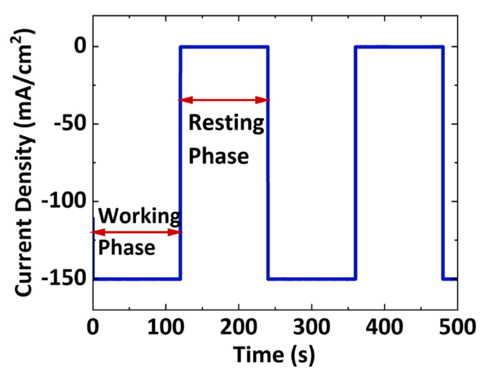
Optimization of Process Conditions

- Li Salt and Concentration
- Li Deposition Substrate
- Solvent
- Proton Donor Type and Concentration
- N_2 Pressure
- Switching Time
- O_2 Content
- Cell Potential
- Reaction Time

Role of Solid Electrolyte Interface (SEI) and Composition of SEI

Modified Autoclave Electrochemical Reactor for High Pressure Experiments





Switching current strategy

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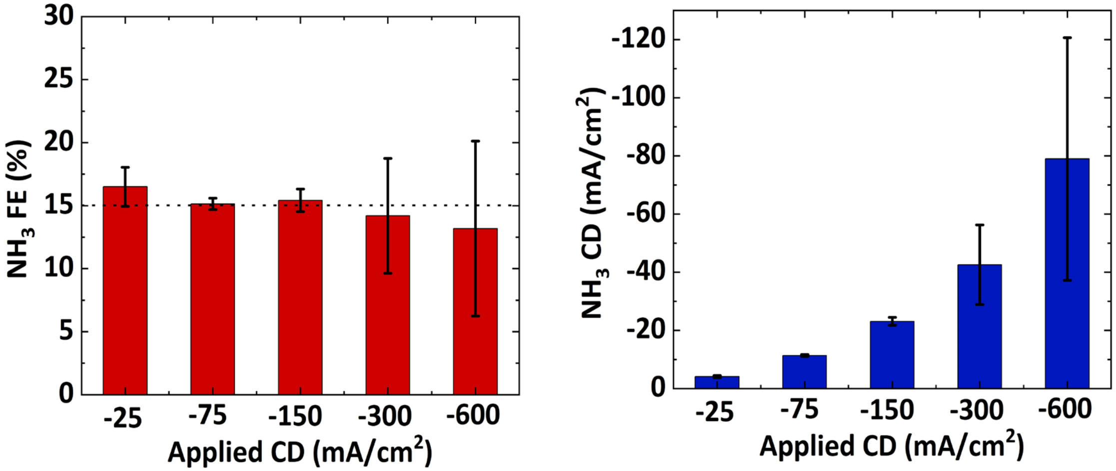
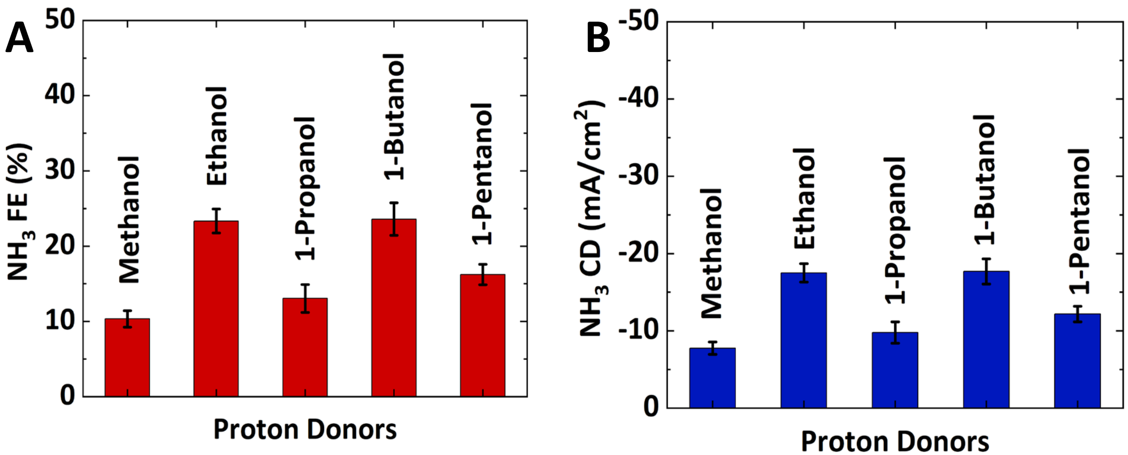
Benchmarking Experiments and Effect of Different Proton Donors

6 bar N_2 Pressure, 0.065 M EtOH Concentration, $LiClO_4$ Switching Current Strategy (2 min, 2 min)



NH_3 Selectivity is independent of the total cell potential



Is there a trend or correlation between NH_3 FE and pKa of donor?

Proton Donor	Methanol	Ethanol	1-Propanol	Butanol	1-Pentanol
pKa	15.5	15.9	16.85	17	16.84

*Note: pKa values are for aqueous systems

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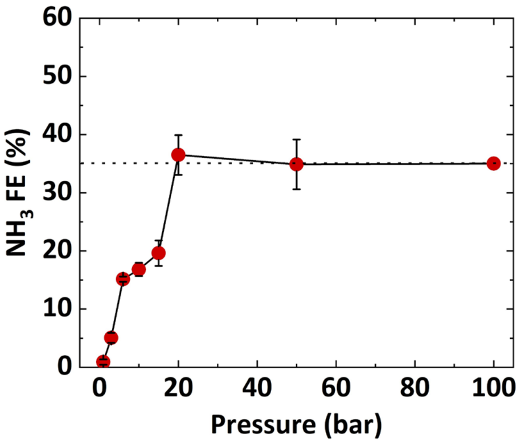
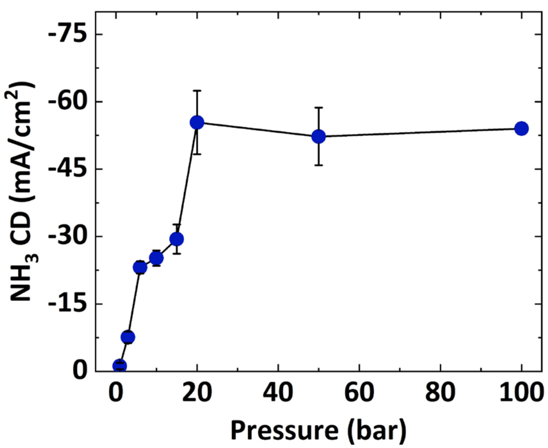
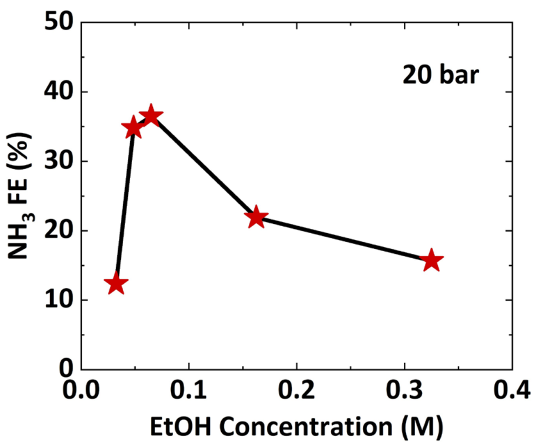
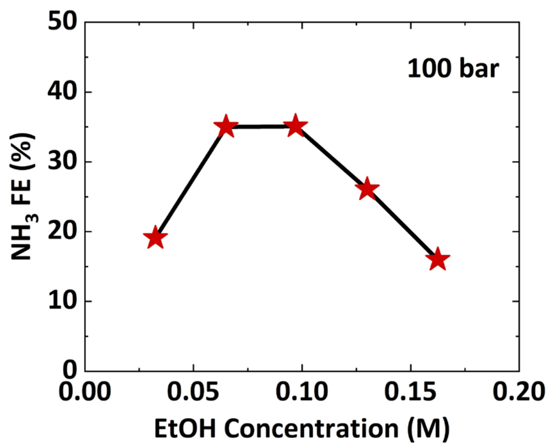
Effect of Pressure and Proton Donor





Maximum NH_3 FE of 35 % is obtained at 20 bar beyond which there is no improvement





At high pressures, increase in proton donor concentration did not improve NH_3 FE

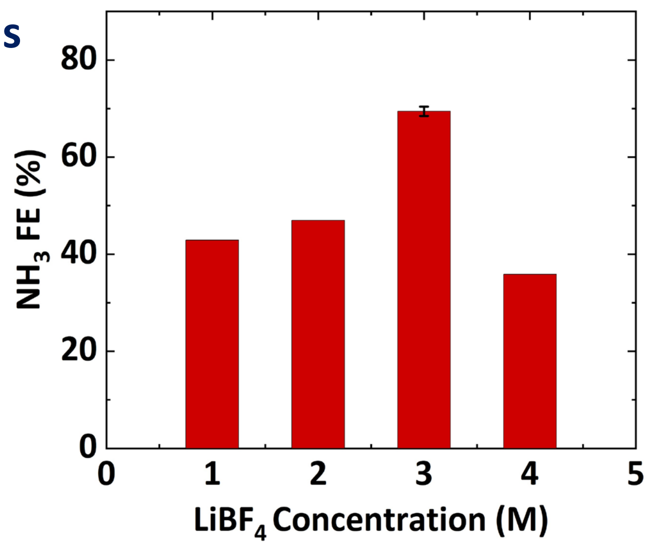
The optimal concentration of EtOH is 0.065 M

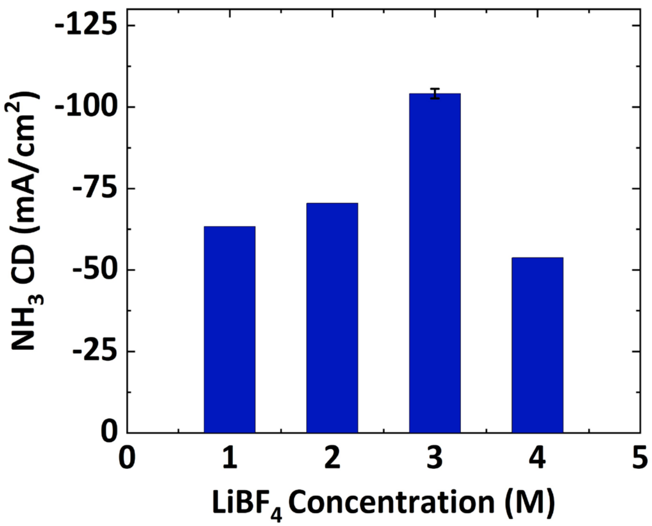
Improving FE beyond 35%

$LiBF_4$ is shown to give a better performance, as the stability of SEI increases with increasing anion size

Optimal Conditions

- 20 bar N_2 Pressure
- 0.065 M EtOH
- -150 mA/cm²
- 2 min, 2min

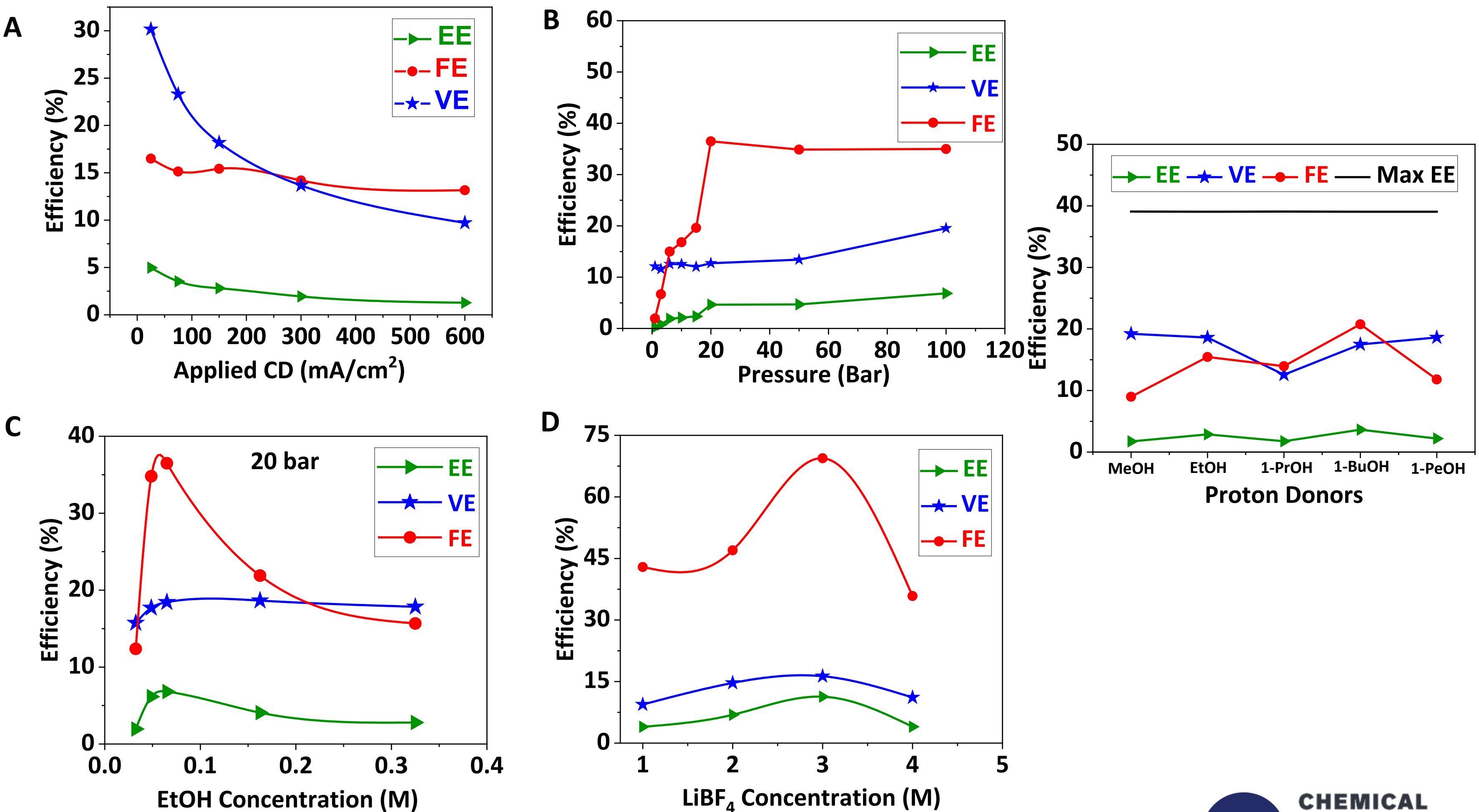




70 % NH_3 FE and ~-100 mA/cm² NH_3 CD using 3 M $LiBF_4$

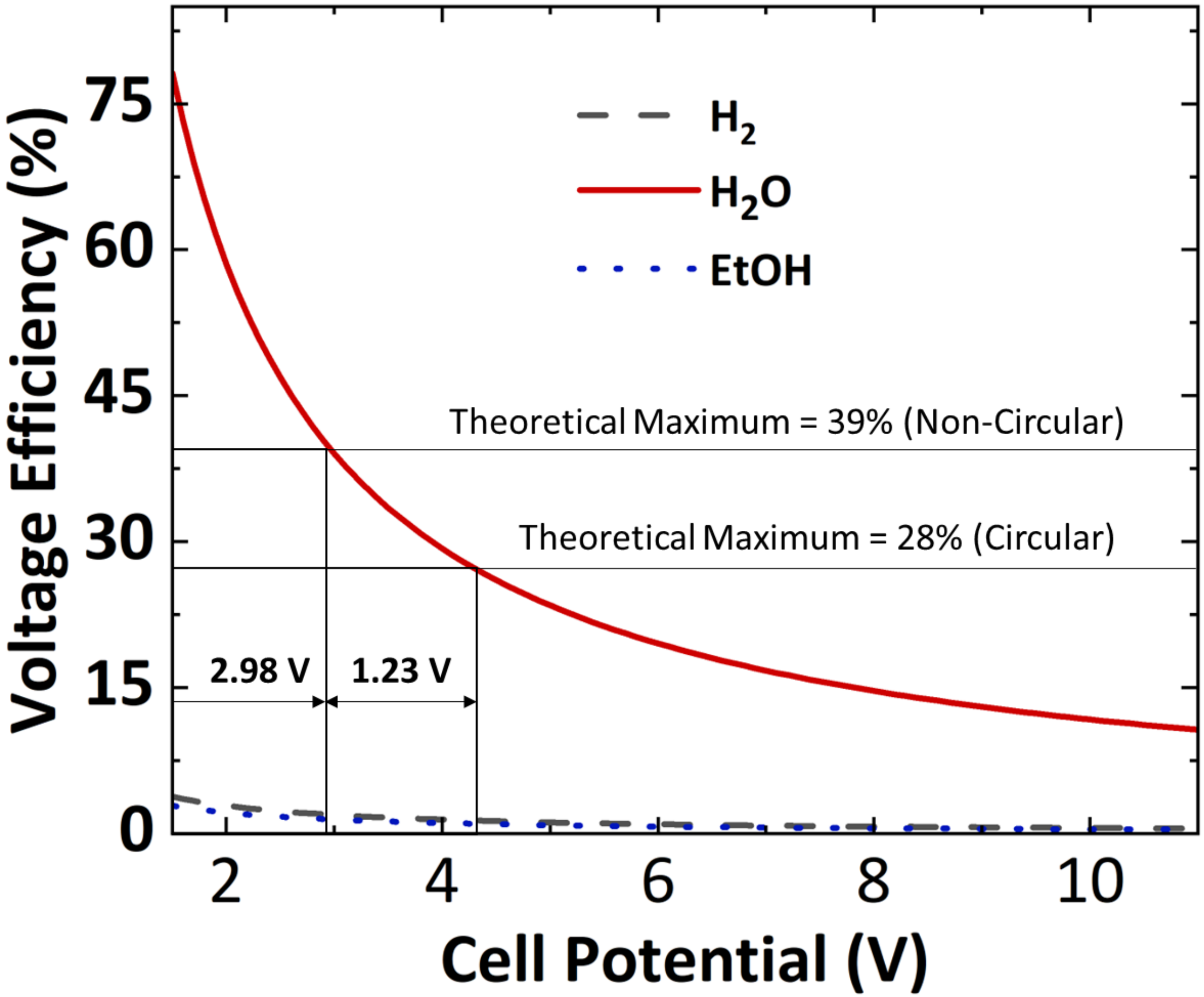
Energy Efficiencies

Energy Efficiency = Voltage Efficiency x Faradaic Efficiency

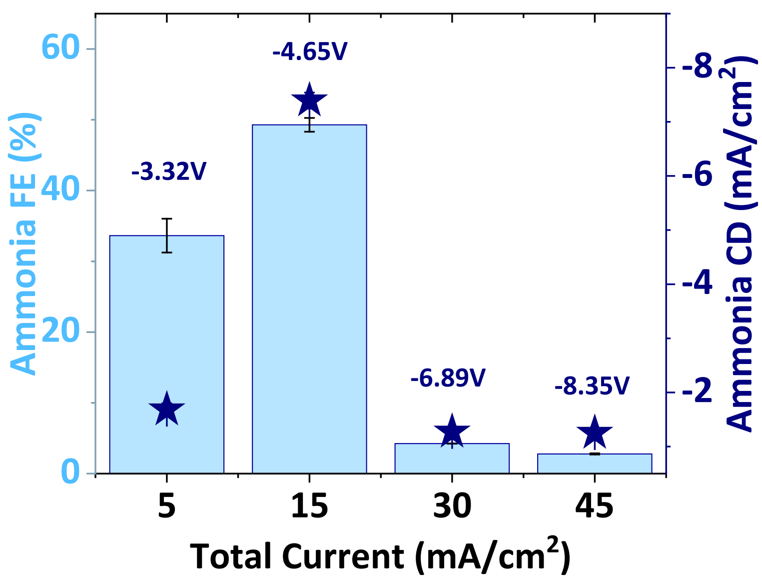


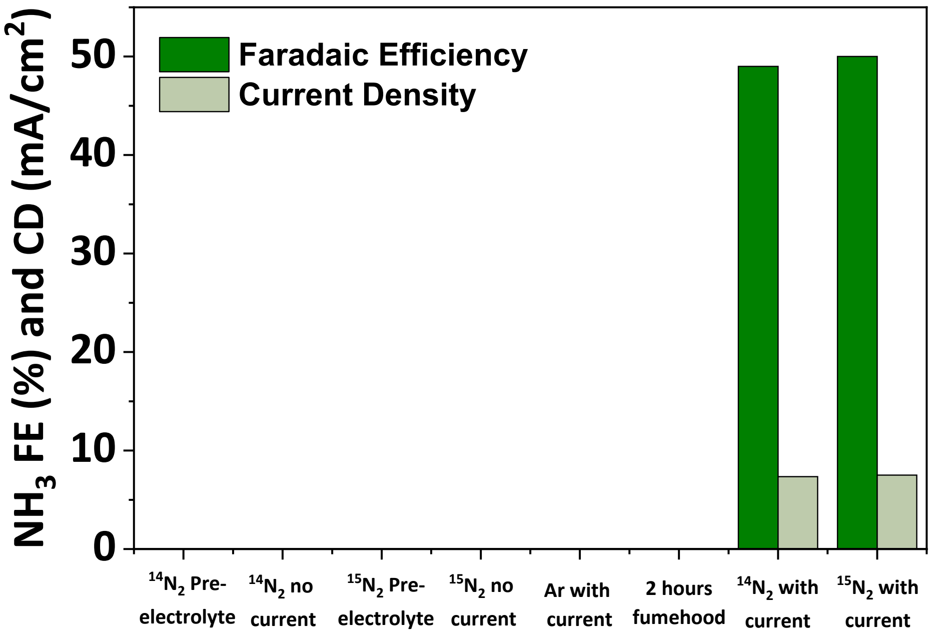
Several Ways to Report Energy Efficiencies

$$\text{Voltage Efficiency} = \frac{\text{Equilibrium Potential } (NH_3/N_2, HX)}{\text{Cell Voltage } (N_2, HX/NH_3)}$$



Exploring Calcium as a mediator for NH_3 Synthesis





At higher currents, like -30mA/cm² and -45 mA/cm², the cell voltage increases rapidly which can electrochemically degrade solvent and form unstable SEI

NMR quantification, isotope labelling, and control studies confirmed that ammonia is forming from N_2 and not because of contamination.

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Metal Nitride as a Mediator for the Electrochemical Synthesis of NH_3

Ishita Goyal,[#] Nishithan C. Kani,[#] Samuel A. Olusegun, Sreenivasulu Chinnabattigalla, Rajan R. Bhawnani, Ksenija D. Glusac, Aayush R. Singh,* Joseph A. Gauthier,* and Meenesh R. Singh*

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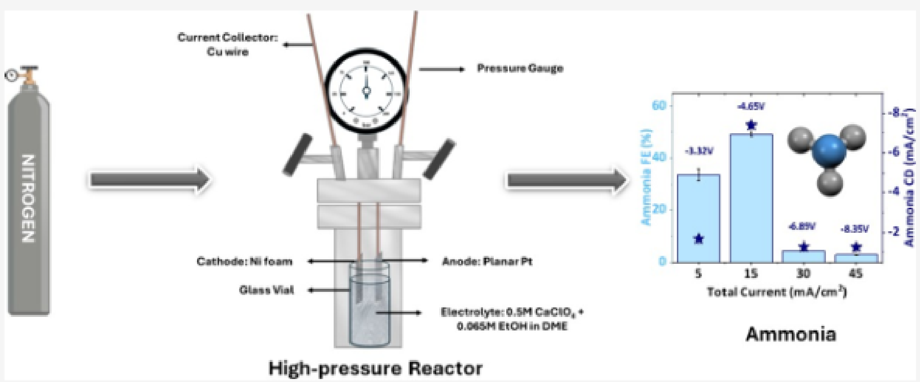
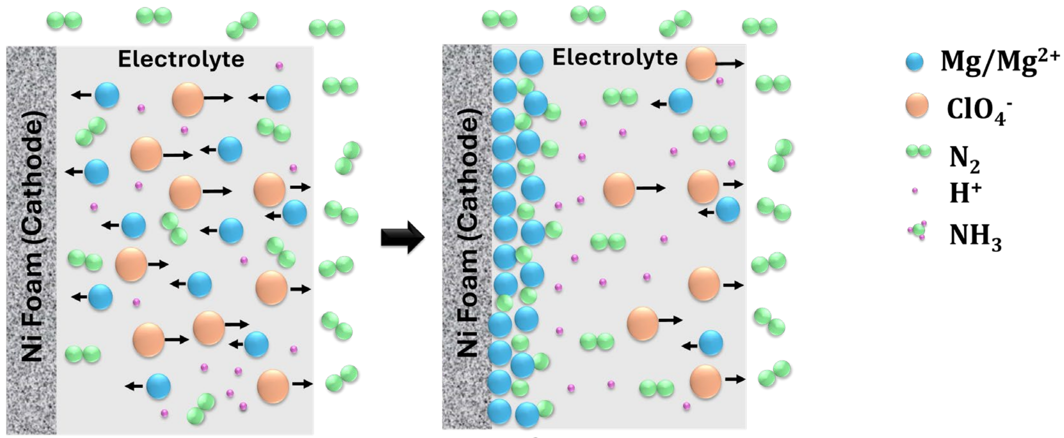
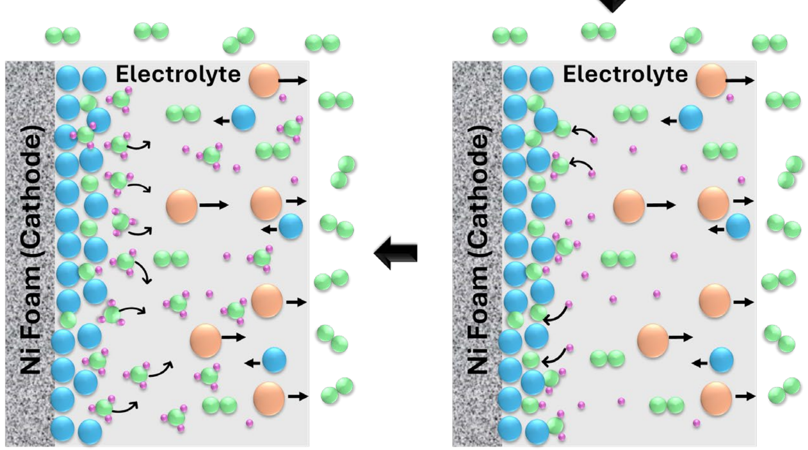


Exploring Mg as a mediator for NH_3 Synthesis



$$Mg^{2+} + 2e^- \rightarrow Mg_{(s)}$$

$$6Mg_{(s)} + N_{2(aq.)} \rightarrow 2Mg_3N_{2(s)}$$

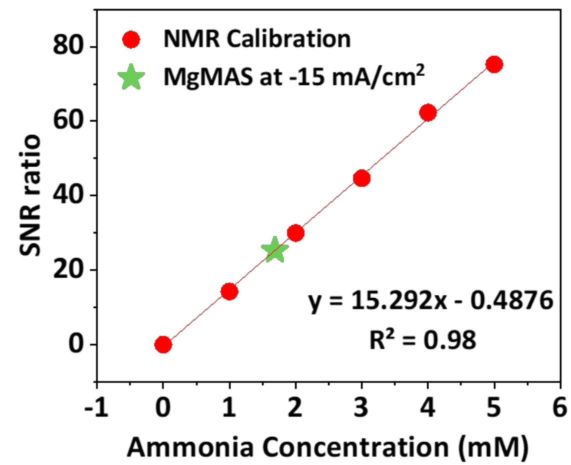


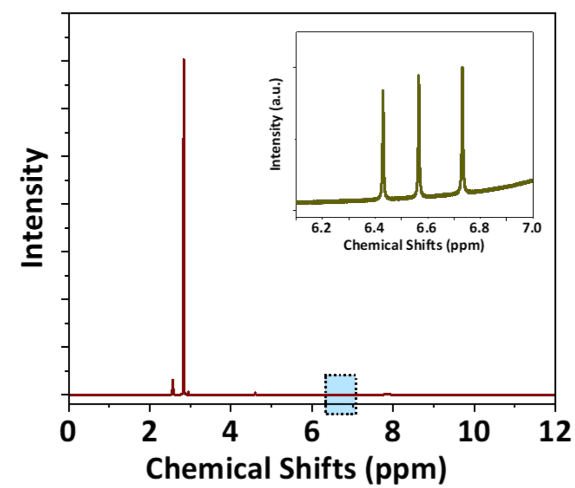
$$Mg_3N - NH_3^* \rightarrow Mg_3N^* + NH_{3(aq.)}$$

$$Mg_3N_{2(s)} + H^+ + e^- \rightarrow Mg_3N - NH^*$$

$$Mg_3N - NH^* + H^+ + e^- \rightarrow Mg_3N - NH_2^*$$

$$Mg_3N - NH_2^* + H^+ + e^- \rightarrow Mg_3N - NH_3^*$$





~ 27% FE achieved from MgMAS system at 15mA/cm² total CD

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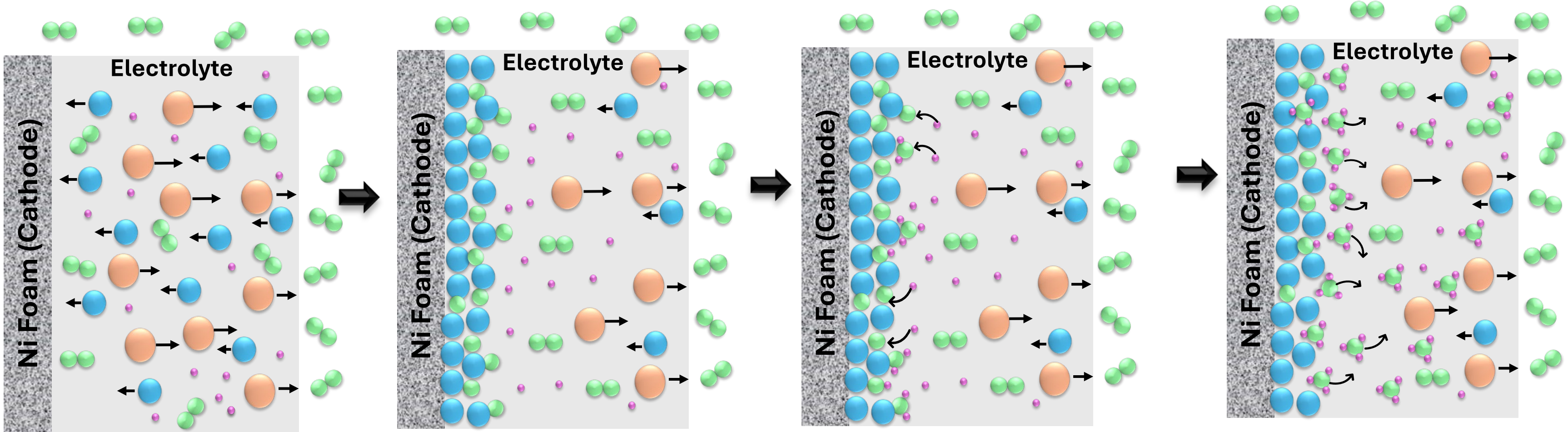
Exploring Mg as a Mediator

Magnesium-mediated NH_3 synthesis



$$Mg^{2+} + 2e^- \rightarrow Mg_{(s)}$$

$$6Mg_{(s)} + N_{2(aq.)} \rightarrow 2Mg_3N_{2(s)}$$

$$Mg_3N_{2(s)} + H^+ + e^- \rightarrow Mg_3N - NH^*$$

$$Mg_3N - NH^* + H^+ + e^- \rightarrow Mg_3N - NH_2^*$$

$$Mg_3N - NH_2^* + H^+ + e^- \rightarrow Mg_3N - NH_3^*$$

$$Mg_3N - NH_3^* \rightarrow Mg_3N^* + NH_{3(aq.)}$$

Mg/Mg^{2+} ClO_4^- N_2 H^+ NH_3

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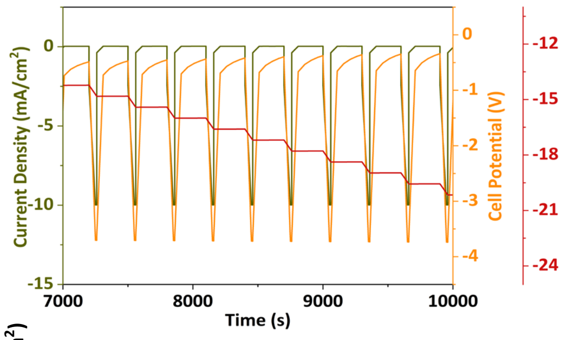
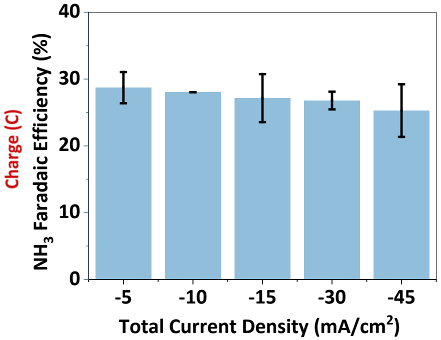
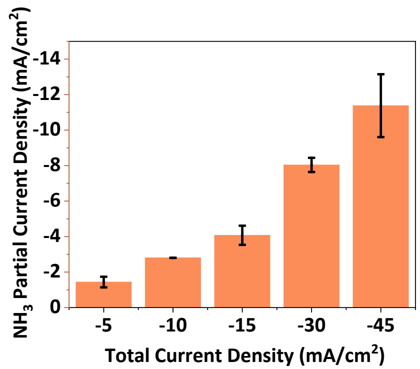
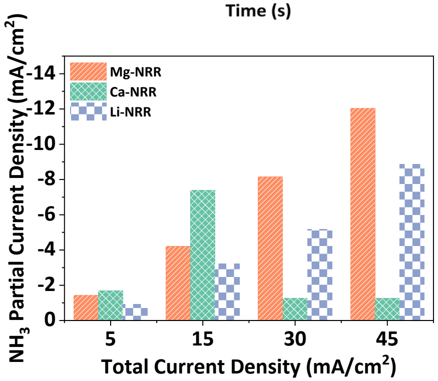
Performance of Mg-MAS System

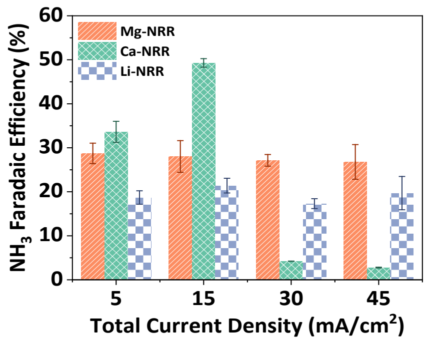


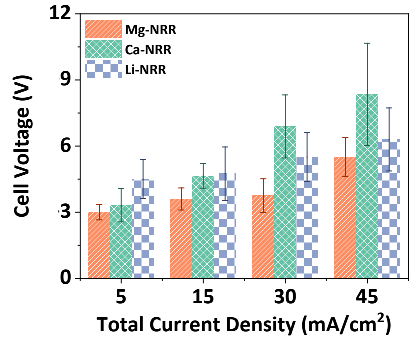




$Mg(ClO_4)_2$ in DMF + 0.065M EtOH
6 Bar N_2
Switching Current
~27% FE







- Solvent Stability
- Conductivity
- Salt Concentration

NH_3 selectivity and ratio of Mg protolysis and Mg_3N_2 protolysis is independent of the applied potential

RESEARCH ARTICLE

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Magnesium-Mediated Electrochemical Synthesis of Ammonia

*Ishita Goyal, Vamsi V. Gande, Rajan R. Bhawnani, Rebecca Hamlyn, Ahmed A. Farghaly, and Meenesh R. Singh**

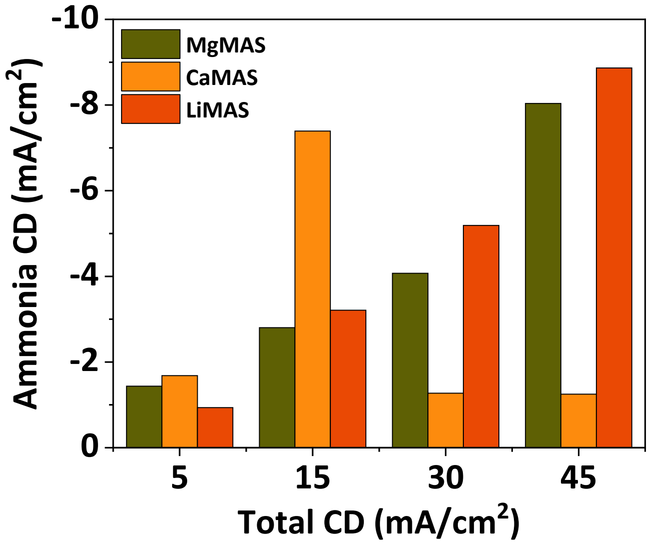
Metal-mediated electrochemical synthesis of ammonia (NH_3) is a promising method to activate N_2 at room temperature. While a Li-mediated approach has been optimized to produce NH_3 at high current density and selectivity, Li's scarcity and its highly negative plating potential limit scalability and energy efficiency. Alternative mediators have been proposed, but only Ca has shown some promise, achieving ≈50% Faradaic efficiency (FE), though requiring voltages beyond −3 V. Here, we report a Mg-mediated nitrogen reduction reaction (Mg-NRR), where N_2 is activated on Mg to form Mg_3N_2, followed by protolysis to release NH_3 and regenerate Mg. A notable NH_3 FE of 25.28 ± 3.80% is achieved at a current density of −45 mA cm^{-2}, corresponding to an NH_3 partial current density of −11.30 ± 1.77 mA cm^{-2} under 6 bar N_2. Isotope-labeled experiments confirm that NH_3 originates from N_2, with similar FE (25.15 ± 1.01%). Importantly, NH_3 production is demonstrated at a total cell potential as low as −3 V. This Li-free Mg-NRR system offers key advantages, including lower energy input and use of earth-abundant materials, making it a scalable route for sustainable NH_3 synthesis.

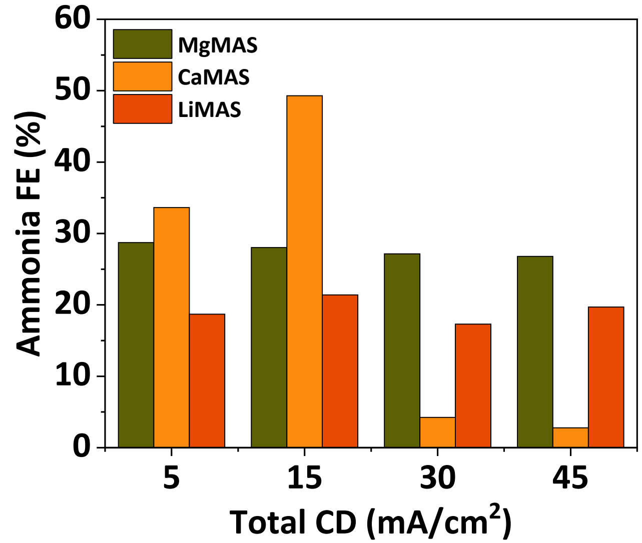
1. Introduction

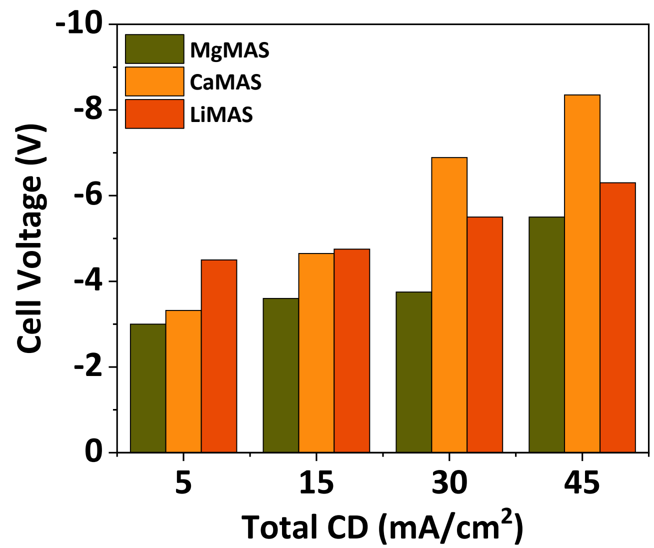
nearly 100%, achieved through the use of imide-based Li salts.[9] Additionally, current densities as high as ≈−700 mA cm^{-2} have been reported. Fu et al.[10] advanced this method further by developing a continuous flow process, achieving a 61% NH_3 FE via hydrogen oxidation on a Pt-Au alloy anode.

Despite these advancements, Li-NRR still suffers from poor energy efficiency, substantially lower than that of the traditional Haber-Bosch process,[3] primarily due to the highly reducing electroplating potential of Li (≈−3.04 V versus SHE).[3] Moreover, the long-term stability of Li-NRR at higher current densities is compromised due to the electrolyte degradation, which impairs Li recovery, and the high cost of Li salts makes the process economically unfeasible. Selecting a metal with a lower reducing electroplating potential could significantly enhance energy efficiency. These limitations underscore the need to explore alternative metal-mediated systems that can offer improved stability and cost-effectiveness.

Comparison of LiMAS, CaMAS, MgMAS







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Professor
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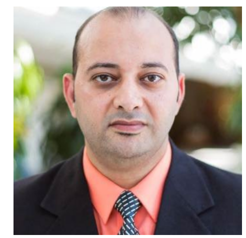
General Ammonia

Mitchell Shields
General Ammonia



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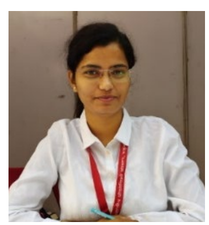

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Questions?

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