

Research Highlight

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Proton shuttle: a key for efficient ammonia electrosynthesis

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Ammonia (NH₃) is one of the essential feedstocks for fertilizers, pharmaceuticals, polymers and other chemicals, as well as an ideal zero-carbon energy carrier, with a global market of ~350 million metric tons per year by 2050^[1]. The industrial synthesis of NH₃ by Haber-Bosch process under high pressure (i.e., 150 to 200 bar) at elevated temperatures (i.e., 350 to 450 °C) consumes a huge amount (i.e., ~1%) of global energy every year, leading to a 1.3% of global CO₂ emission^[2]. Alternatively, the electrochemical nitrogen reduction reaction using lithium as medium (Li-NRR) in electrolytes for NH₃ synthesis has proven to be a zero-carbon emission process, with a highly desired perspective^[3,4]. Generally, the Li-NRR for the NH₃ synthesis contains three steps [Figure 1A]: (1) the Li⁺ in electrolyte is electrochemically reduced to Li⁰ on the cathode; (2) the Li⁰ dissociates N₂ to generate lithium nitride (e.g., Li₃N); (3) the lithium nitride is further protonated by proton source, offering NH₃ product and leaving Li⁺ ions to repeat the catalytic cycle^[5]. The required sacrificial solvent (e.g., ethanol) as the proton sources in nonaqueous electrolytes strongly hampers the industrialization of Li-NRR for continuous NH₃ synthesis over the past three decades.

A proton shuttle, a type of functional molecule that favors proton transportation and can be fully recycled, proposed for solving the problem of sacrificial proton sources is of significance as it allows the proton for



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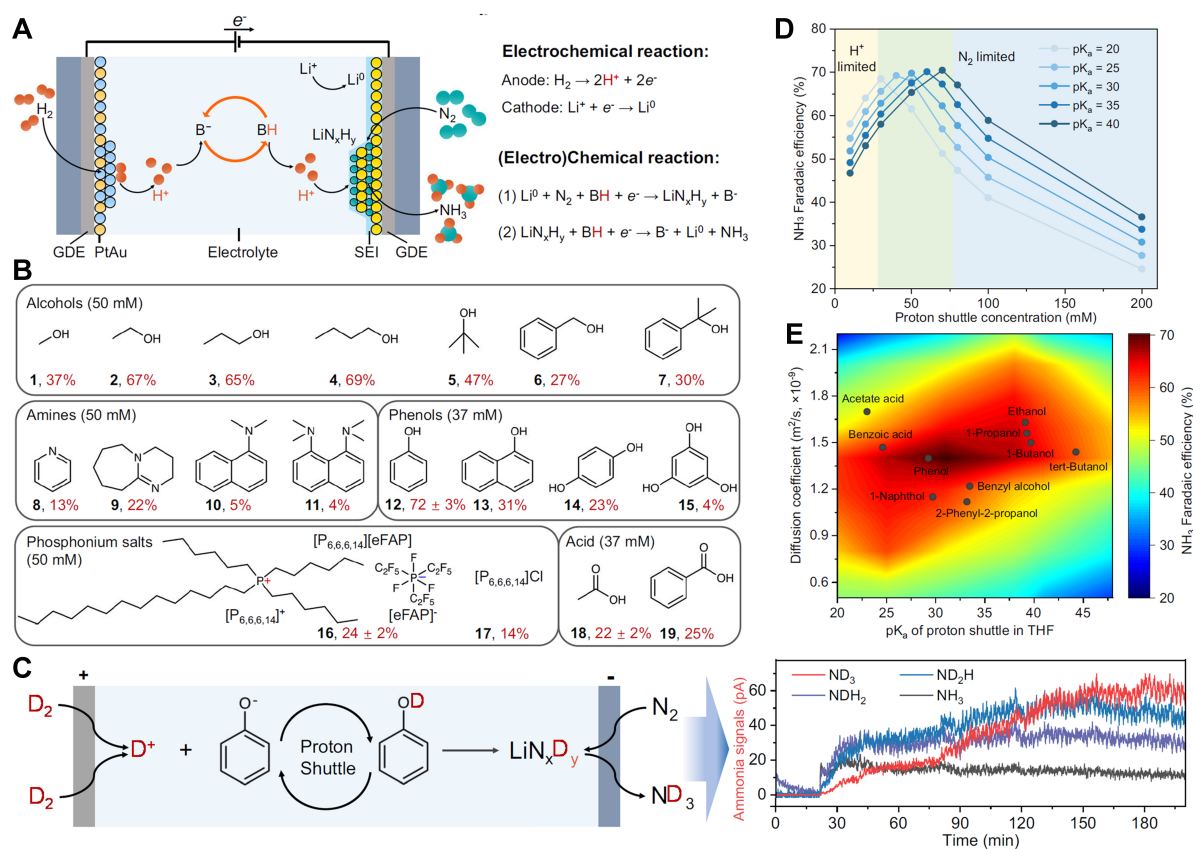


Figure 1. (A) Schematic proton-shuttling process for lithium-mediated ammonia synthesis in a continuous flow reactor; (B) Ammonia faradaic efficiencies for a variety of proton shuttles by passing a total charge of 700 C (over 2.5 h) with the constant potential cycling ($-6 \text{ mA}\cdot\text{cm}^{-2}$ for 1 min and then $0 \text{ mA}\cdot\text{cm}^{-2}$ for 1 min); (C) Demonstration of the ability of phenol for proton shuttling; (D) A 1D plot of ammonia FE vs. concentrations of proton shuttle with different pK_a in THF; (E) Heatmap of the predicted ammonia FE as a function of the pK_a of proton shuttle (x-axis) and diffusion coefficient (y-axis). (This figure is reproduced with permission from Fu *et al.*^[8]) FE: Faradaic efficiency; THF: tetrahydrofuran.

continuous Li-NRR on the cathode coming from a sustainable hydrogen oxidation reaction (HOR) of external H_2 gas on the anode of an electrocatalysis system. The first exploration of proton shuttles was performed by Krishnamurthy *et al.*, who report that 1-butanol is identified as one of the most effective proton shuttles [faradaic efficiency (FE) of 15.6%]^[6]. However, they later clarified that the enhanced Li-NRR performance was mainly due to the change property of the solid-electrolyte interphase in the presence of proton shuttles. Recently, Suryanto *et al.* developed the phosphonium-based salts (e.g., $[\text{P}_{6,6,6,14}][\text{eFAP}]$) as the proton shuttle for Li-NRR over three days of continuous operation, and confirmed the protonation reversibility of $[\text{P}_{6,6,6,14}]^+$, unfortunately, by an *ex-situ* simulated experiment reacting with acetic acid^[7]. It leaves an unclarified proton shuttling mechanism in the real Li-NRR process for ammonia electrosynthesis, causing an unknown design strategy for effective and easily accessible proton shuttles.

The study by Fu *et al.* fills some of these gaps^[8]. Specifically, by combining detailed Li-NRR process analysis and functional interpretations, the authors summarize the basic requirements and principles for designing effective proton shuttles: (1) containing functional groups (e.g., $-\text{OH}$, $-\text{COOH}$, and $-\text{CHO}$) or specific moiety (e.g., α -hydrogen atom and $-\text{CH}_2-$) that can donate/accept a proton; (2) a proper acid dissociation constant (pK_a) to balance protonation and minimize side reaction in electrolytes; (3) enabling form a functional solid-electrolyte interphase on cathode to allow H^+ and Li^+ diffusion; (4) good electrochemical

stability and high chemical stability; (5) an optimal diffusion rate in electrolytes that allows the control of the amount of available protons for reacting with lithium nitride on the cathode surface; (6) excellent compatibility with the catalysts and electrolytes in Li-NRR system; Following the essential elements proposed in principles, the authors carefully evaluate dozens of potential proton shuttles in a continuous-flow reactor; it shows that phenol offers the highest performance with $72\% \pm 3\%$ FE, alcohols are good shuttles ($27\% \sim 69\%$ FE), amines and carboxylic acids are inefficient shuttles ($4\% \sim 24\%$ FE), and phosphonium salts remain in the mediate [Figure 1B], offering a conclusion: the dependence of the Li-NRR performance on the pK_a and diffusion coefficient of proton shuttles. This comprehensive exploration and evaluation on proton shuttles solve one of the hardest but the most important tasks in Li-NRR process. It is of great value to the scientific study and the industrialization of Li-NRR for zero-carbon emission NH_3 synthesis, which are strongly supported by the later significant breakthroughs in long-term continuous ammonia electrosynthesis from Li *et al.*^[9,10].

A key finding of this work is the identification of the proton shuttling behavior in the real Li-NRR process by operando isotope-labeled mass spectrometry, coupled with utilizing the deprotonated proton shuttles (B^-) to evaluate the proton transfer capability. Using deuterium (D_2) oxidation reaction (DOR) as the proton (D^+) source, the classically hypothesized proton shuttling mechanism was skillfully *in-situ* confirmed: D^+ is shuttled by phenol (PhOH) during Li-NRR, and it offers the main ammonia product gradual changing from NH_3 , NH_2D and NH_1D_2 , finally to a sole ND_3 owing to the protonation of PhO^- to $PhOD$ [Figure 1C]. The protonation and deprotonation behavior of proton shuttles (i.e., PhO^-) was respectively clarified by using a PhOLi precursor, which converts to PhOH in real Li-NRR process. This work provides unambiguous evidence of the proton shuttling using PhOH as a proof-of-concept demonstration for the first time, setting an excellent example for future researchers on developing alternative novel proton shuttles.

While searching for the mechanisms enabling PhOH to be the efficient proton shuttle, the authors could unexpectedly identify that the pK_a and the size-related diffusivity codetermine the Li-NRR performance: an optimal NH_3 FE would require either acidic but transport-limited proton shuttles or basic but transport-fast shuttles [Figure 1D and E]. The pK_a determines the protonation-deprotonation kinetic of proton shuttles on the anode and cathode surfaces, while the size of proton shuttles affects their diffusion mobility between the anode and cathode. These findings highlight the intense correlation between pK_a and size-related diffusivity in proton shuttling, and they could serve as significant guidelines for developing novel proton shuttles.

This study provides a detailed analysis on sieving efficient proton shuttles and clarifies the proton shuttling behavior in the real Li-NRR process. The detailed mechanistic insights and the demonstration of two key factors [i.e., the pK_a in tetrahydrofuran (THF) and the size-related diffusivity] mark a significant advancement in our understanding of proton shuttles. However, several questions remain open. A key area for further investigation is elucidating the universality of the proposed design principle in various solvents of electrolytes (such as ether-based solvents), other than THF. Additional catalytic kinetic exploration needs to be performed to clarify the way how the instinct property of solvent affects the H^+ limited and N_2 limited step during the Li-NRR process [Figure 1D]. Moreover, even though the theoretical reaction steps were clearly presented [Figure 1A], the practical reaction mechanism, in particular, how the protons obtained from the deprotonation of proton shuttle react with lithium nitride, remains enigmatic. It indicates that an urgent and significant breakthrough in the Li-NRR mechanism is highly desired, potentially through the use of advanced operando technologies (e.g., *in-situ* transient absorption spectroscopy, operando isotope-labeled mass spectrometry, *etc.*). Besides that, the large operation voltage of Li-NRR (i.e., ~ 4.3 V^[8], much higher than the standard electrode potential of Li, 3.045 V) shows a low energy efficiency of the current Li-NRR process. Further development on promising electrolytes and electrode materials for the

industrialization of Li-NRR with low energy consumption is important. All these questions are required to be addressed in future studies in order to set up the way for sustainable and environmentally friendly ammonia production.

DECLARATIONS

Authors' contributions

Made substantial contributions to conception and design of the study and performed data analysis and interpretation: Wang, Z., Su, B.L.

Performed data acquisition and provided administrative, technical, and material support: Wang, Z., Guan, Z.L.

Availability of data and materials

Not applicable.

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Conflicts of interest

Wang, Z., a Junior Editorial Member of *Chemical Synthesis*, was not involved in the editorial process of the work. Su, B.L., Editor-in-Chief of *Chemical Synthesis*, was not involved in the editorial process of the work. While the other author has declared that he has no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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