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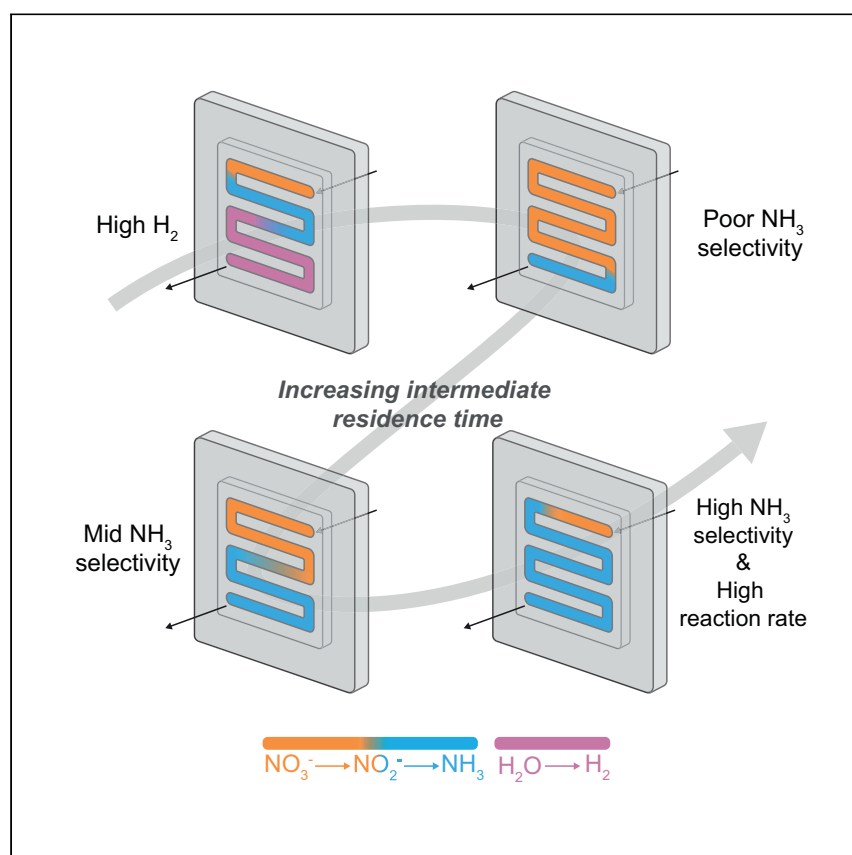
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# Article

## Sequential electrocatalytic reactions along a membrane electrode assembly drive efficient nitrate-to-ammonia conversion



Yuan et al. produce ammonia from nitrate via a two-step sequential reaction in a membrane electrode assembly, utilizing flow rates to control reactivity at elevated current densities. This work shows that controlling the intermediate residence time and traditional engineering principles can substantially boost selectivity, even for simple catalysts.

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### Highlights

>90% selectivity and 1.8 A for nitrate reduction to ammonia on unmodified copper catalyst

Membrane electrode assembly overcomes the limitations of a sequential mechanism

Residence time of intermediates determines product selectivity

Intermediate residence time can be tuned by altering system operation parameters

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## Article

## Sequential electrocatalytic reactions along a membrane electrode assembly drive efficient nitrate-to-ammonia conversion

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## SUMMARY

Electrochemical ammonia (NH<sub>3</sub>) synthesis from nitrate (NO<sub>3</sub><sup>−</sup>) offers a promising greener alternative to the fossil-fuel-based Haber-Bosch process to support the increasing demand for nitrogen fertilizers while removing environmental waste. Previous studies have mainly focused on designing catalysts to promote the direct conversion (NO<sub>3</sub><sup>−</sup> → NH<sub>3</sub>) while suppressing the two-step pathway (NO<sub>3</sub><sup>−</sup> → NO<sub>2</sub><sup>−</sup> → NH<sub>3</sub>). We hypothesize that efficient nitrate reduction is possible on simple catalysts by instead promoting the two-step reaction and using chemical reactor principles in a membrane electrode assembly, despite NO<sub>2</sub><sup>−</sup> intermediates. Here, we use an unmodified copper catalyst and control reactivity through current density, flow rate, and electrolyte recycling. Balancing the electrolyte flow rate with current density results in ideal residence times for NO<sub>2</sub><sup>−</sup>, allowing for 91% FE<sub>NH<sub>3</sub></sub> in a 5 cm<sup>2</sup> electrolyzer with a NO<sub>3</sub><sup>−</sup> to NH<sub>3</sub> partial current of 1.8 A. This work shows that traditional engineering principles can substantially boost the NO<sub>3</sub> reduction reaction, even for simple catalysts.

## INTRODUCTION

Current nitrogen fertilizer production is highly fossil fuel based, leading to considerable CO<sub>2</sub> emissions. The Haber-Bosch process converts nitrogen gas (N<sub>2</sub>) with hydrogen (H<sub>2</sub>) (derived from natural gas) to ammonia (NH<sub>3</sub>) under high temperatures and high pressures (Figure 1A). Approximately 2% of global energy consumption and 40 Mt of CO<sub>2</sub> emissions are associated with nitrogen fertilizer production annually.<sup>1</sup> Additionally, large-scale Haber-Bosch facilities centralize production to lower costs, leading to increased energy consumption from transportation to the decentralized end-use locations. Thus, there is an urgent need to develop sustainable ammonia production routes using renewable energy sources as the input. As a result, electrochemical ammonia synthesis routes have gained attention.

Multiple approaches have been developed for the electrochemical reduction of N<sub>2</sub> (N<sub>2</sub> reduction reaction [NRR]), including an NRR in the aqueous system<sup>2–9</sup> and lithium-mediated N<sub>2</sub> reduction in the organic solution (Li-NRR).<sup>10–16</sup> At present, the aqueous NRR suffers from the inert nature of N<sub>2</sub> and is being kinetically outcompeted by the hydrogen evolution reaction (HER).<sup>8,17</sup> Although different strategies have been applied to break scaling relationships between the NRR and the HER, the current aqueous performance is still limited at ~10 mA cm<sup>−2</sup>. Additionally, the low yield of NRR and improper experimental protocols have led to numerous false positives due to contamination.<sup>7,18–21</sup> On the other hand, Li-NRR utilizes the highly

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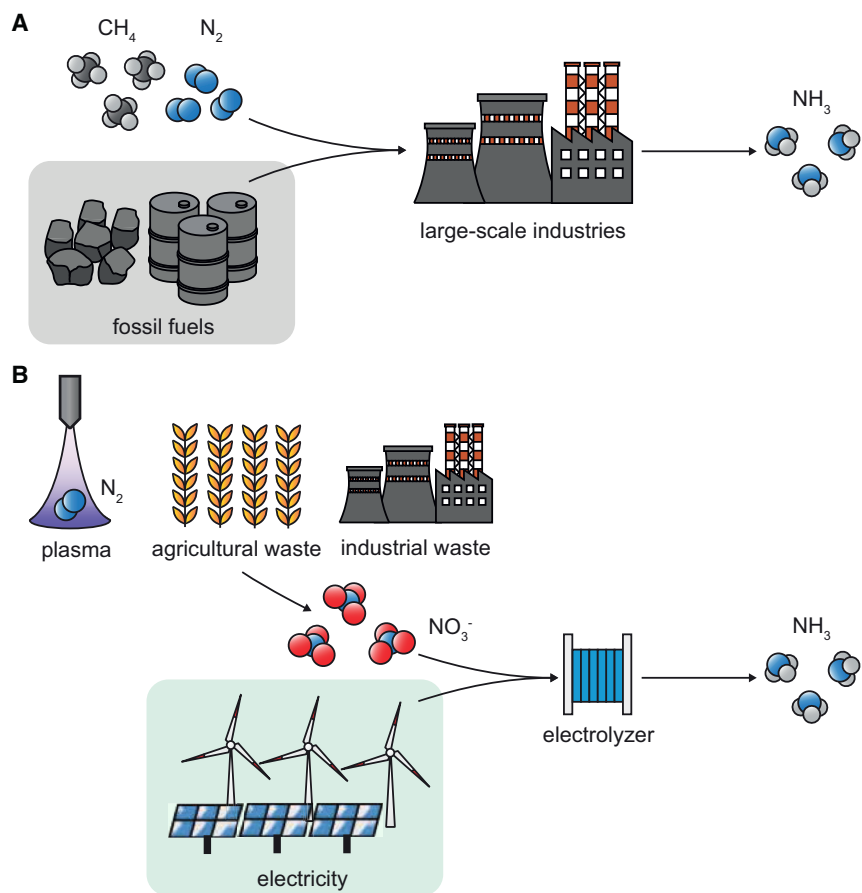
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**Figure 1. Comparison between traditional ammonia production and the proposed electrochemical alternative**

(A) Current Haber-Bosch process for ammonia production, which requires  $\text{N}_2$  and  $\text{CH}_4$  as starting materials and fossil fuels as the energy source.

(B) Proposed electrochemical-based ammonia production with  $\text{NO}_3^-$  as the reactant and renewable electricity as the energy source.

active lithium metal to react with  $\text{N}_2$ .  $\text{Li}^+$  is electrochemically reduced into metallic lithium metal, which later forms  $\text{Li}_3\text{N}$  upon contact with  $\text{N}_2$ .  $\text{Li}_3\text{N}$  then reacts with proton sources to form  $\text{NH}_3$  and  $\text{Li}^+$ . The Li-NRR can achieve nearly 100% Faradaic efficiency (FE) to ammonia at industrial-relevant current densities.<sup>16</sup> However, high full-cell voltages associated with the Li-NRR lead to high energy consumption.<sup>14</sup>

Nitrate ( $\text{NO}_3^-$ ) can be an alternative nitrogen source for fertilizer synthesis.  $\text{NO}_3^-$  is more reactive than  $\text{N}_2$  and is considered an environmental pollutant, giving its removal an added benefit<sup>22,23</sup> (Figure 1B). Wastewater from agriculture, explosives factories, and mine industries contain a considerable amount of  $\text{NO}_3^-$ , especially nuclear wastewater.<sup>22</sup> The presence of  $\text{NO}_3^-$  in water causes eutrophication in aqueous ecosystems and threatens drinking water safety. Thus, removing  $\text{NO}_3^-$  from water using electricity is an attractive approach for waste remediation, particularly if it can also be converted into a valuable compound and complete the nitrogen cycle. Previous studies have investigated the electrochemical reduction of  $\text{NO}_3^-$  into  $\text{N}_2$ ,<sup>24,25</sup> but the direct electrochemical  $\text{NO}_3^-$  conversion to  $\text{NH}_3$  ( $\text{NO}_3\text{RR}$ ) has gained more traction in recent years.<sup>24,26–35</sup> A few studies have discussed the unique potential of the  $\text{NO}_3\text{RR}$  in future sustainable development.<sup>22,23,36</sup> We take the view that electrochemical  $\text{N}_2$  reduction to  $\text{NH}_3$  and

electrochemical  $\text{NO}_3^-$  conversion to  $\text{NH}_3$  are two very different reactions and fields of interest. For ammonia production, these two fields have different markets and targets. NRRs (both aqueous and Li-mediated) would act as a competitor to the current Haber-Bosch process. Li-NRR systems have substantial equilibrium cell voltages ( $>3$  V), which makes them fundamentally tough to compete against renewable  $\text{H}_2$  + Haber-Bosch. Conversely, the  $\text{NO}_3\text{RR}$  requires lower energy to perform. In our view, the  $\text{NO}_3\text{RR}$  has the potential now as a waste stream mediator and efficient ammonia production route, albeit at smaller maximum market sizes than potential NRRs.

Numerous previous studies have reported  $\text{NO}_3\text{RRs}$  in the laboratory-scale batch reactor—typically called an H-cell. On many electrocatalytic surfaces, however,  $\text{NO}_3^-$  can be reduced to either nitrite ( $\text{NO}_2^-$ ) or  $\text{NH}_3$  ( $\text{NO}_3^- \rightarrow \text{NH}_3$ ). Additionally,  $\text{NO}_2^-$  can act as an intermediate for ammonia production such that a two-step reaction occurs ( $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NH}_3$ ). In batch reactor experiments, however, where the reactant concentration of a well-mixed vessel becomes homogeneous, it is important to catalytically maximize the single-step reaction  $\text{NO}_3^- \rightarrow \text{NH}_3$  to reach a high FE and current densities ( $j$ ) toward  $\text{NH}_3$ . Otherwise,  $\text{NO}_2^-$  that is produced at the electrode will diffuse back into the bulk electrolyte, leading to a lower selectivity toward  $\text{NH}_3$ . As a result, many efforts have gone into tuning catalyst compositions and structures to suppress  $\text{NO}_2^-$  formation through bimetallic<sup>26,33</sup> or single-atom catalysts.<sup>27,30</sup> Other works have used a catalytic tandem approach to reduce by-product  $\text{NO}_2^-$  before it can diffuse back into the bulk electrolyte.<sup>32,37</sup>

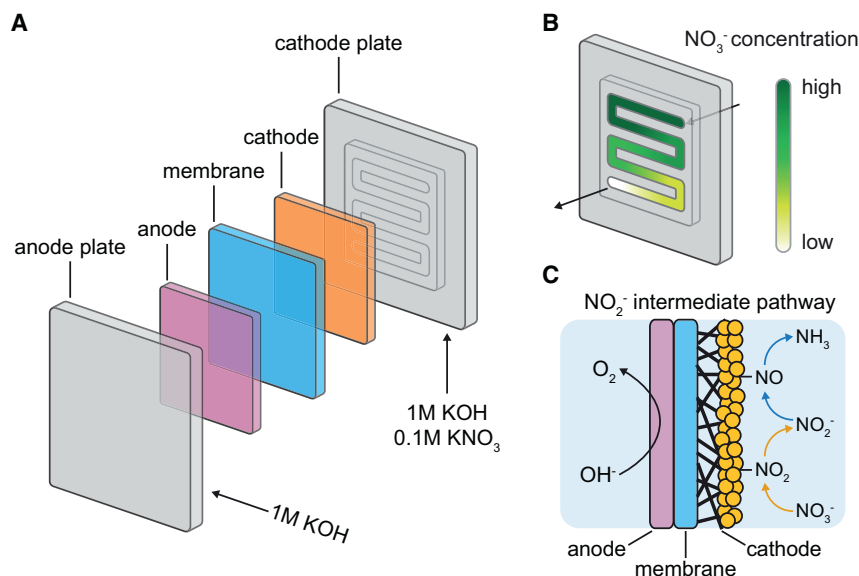
Although great efforts have been put into designing catalysts for the batch reactor environment, comparatively few studies<sup>38–40</sup> have utilized more compact membrane electrode assembly (MEA) configurations that, in the future, are needed to lower cell internal resistance and provide better scalability potential.<sup>41</sup> Other fields in electrolysis<sup>42</sup> have pointed out that (1) knowledge learned from H-cells is not fully transferable to MEAs and (2) catalysts' performances can differ dramatically from H-cell to MEA, especially in product selectivity. Aside from the efficiency and volume benefits of an MEA electrolyzer, the system allows for reagents to flow past the electrodes (Figure 2B) in a much more controlled environment than H-cells. Control over the reagent, by-product, and product concentrations is then much greater and can provide unexplored utility for  $\text{NO}_3\text{RRs}$  by varying operation conditions such as flow rates, flow patterns, and operating modes (circulation vs. single pass).

In this work, we hypothesized that the use of an MEA could overcome the limitations of a sequential reaction mechanism ( $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NH}_3$  in Figure 2C) for  $\text{NO}_3\text{RRs}$ , providing less emphasis on catalyst design and aiding in the faster applicability of the technology. After assembling an MEA system for the  $\text{NO}_3\text{RR}$ , we then explored how operating parameters impact measured nitrite and ammonia FEs for various flow rates and current densities. We found that by taking advantage of the residence time of by-product  $\text{NO}_2^-$ , we achieved near-unity ammonia FEs at current densities of  $395 \text{ mA/cm}^2$ . Our findings suggest that the catholyte flow rate impacts the residence time of reactants/intermediates which alters product selectivity. We further examined the trade-offs between  $\text{NO}_3^-$  full conversion and  $\text{FE}_{\text{NH}_3}$  by comparing recirculating vs. single-pass operations.

## RESULTS

### Electrolyzer setup

To explore the sequential  $\text{NO}_3^-$  conversion in an MEA, the copper catalyst was tested in an MEA with a  $5 \text{ cm}^2$  active area.<sup>43</sup> Copper was sputtered on a carbon



**Figure 2. Schematics of our MEA setup, key characteristics, and key reactions**

(A) The structure of our MEA includes copper on carbon paper as the cathode, a membrane, and a nickel foam as the anode.

(B)  $\text{NO}_3^-$  concentration gradient along the flow field in the MEA.

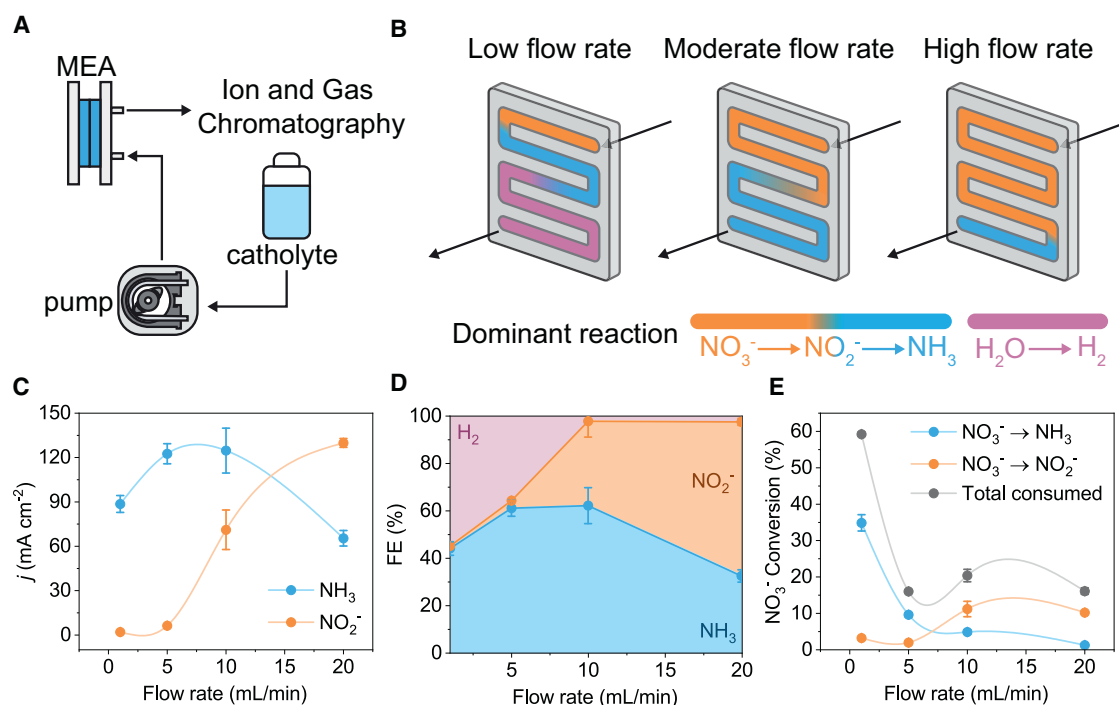
(C)  $\text{NO}_3^-$  conversion to  $\text{NH}_3$  via the two-step sequential pathway.

substrate (Figure S1) as the working electrode with 1 M KOH + 0.1 M  $\text{KNO}_3$  as the catholyte (Figure 2A). A hydrophilic macropore carbon paper was chosen as the substrate to promote mass transport from the aqueous to the electrode.<sup>44</sup> We explored the effect of the catalyst-facing direction, and these data are shown in Figure S4. When copper was placed toward the membrane instead of toward the flow field, the total FE toward  $\text{NO}_3^-$  conversion ( $\text{FE}_{\text{NH}_3} + \text{FE}_{\text{NO}_2^-}$ ) decreased. These results indicate that  $\text{NO}_3^-$  diffusion through the carbon support was limited, resulting in a higher HER when the operating current density is fixed at rates beyond  $\text{NO}_3^-$  transport. Based on catalyst orientation results, the copper catalyst was placed toward the flow field to reduce the distance between the bulk catholyte nitrate and the copper layer. A nickel foam was used as the counter electrode with 1 M KOH as the anolyte. A cation exchange membrane separated the two electrodes. Detailed experimental procedures can be found in the [experimental procedures](#), and pictures of each cell part can be found in Figure S2.

### Analyzing the effects of $\text{NO}_3^-$ residence time on the dominant product formed

At a fixed current density, the location and reactions occurring can be influenced by controlling the flow rate of  $\text{NO}_3^-$  through the MEA cell (Figure 3A). With a high concentration of  $\text{NO}_3^-$ ,  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  (Figure 3B) should be the dominant reaction near the inlet, and a concentration gradient of  $\text{NO}_3^-$  along the flow field should occur (Figure 2B). As  $\text{NO}_3^-$  is converted to  $\text{NO}_2^-$  on copper, the concentration of  $\text{NO}_2^-$  should reach a maximum at a certain point in the flow channel, and the dominant reaction will switch to  $\text{NO}_2^- \rightarrow \text{NH}_3$  (colored in blue in Figure 3B). When  $\text{NO}_2^-$  is fully depleted near the electrode surface, the HER will take over (colored in pink in Figure 3B).

We hypothesized that catholyte flow rates determine the residence time of reactants with a negative correlation, further impacting product distributions. With low flow rates, long  $\text{NO}_3^-$  residence times should lead to fast  $\text{NO}_3^-$  depletion with fast



**Figure 3. Single-pass experiments at  $200 \text{ mA cm}^{-2}$  with different catholyte flow rates**

(A) Schematic of catholyte single-pass experiment with 1 M KOH + 0.1 M  $\text{KNO}_3$  as catholyte.

(B) Schematic of hypothesized dominant reactions along the flow channel.

(C) Partial current densities of  $\text{NO}_2^-$  and  $\text{NH}_3$ .

(D) Faradaic efficiency of  $\text{NH}_3$ ,  $\text{NO}_2^-$ , and  $\text{H}_2$  where area represents FE.

(E) Conversion of  $\text{NO}_3^-$ ,  $\text{NO}_3^-$  to  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  to  $\text{NH}_3$ .

Error bars represent the standard deviation from three replicates.

$\text{NO}_2^-$  accumulation (Figure 3B, first image). The dominant reaction is expected to switch from  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  to  $\text{NO}_2^- \rightarrow \text{NH}_3$  close to the inlet. Once  $\text{NO}_2^-$  is fully consumed, the HER should dominate the flow channel near the outlet. Thus,  $\text{H}_2$  and  $\text{NH}_3$  are expected as major products at low catholyte flow rates. At moderate flow rates, the dominant reaction should switch from  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  to  $\text{NO}_2^- \rightarrow \text{NH}_3$  further away from the inlet since the residence time of  $\text{NO}_3^-$  is shortened (Figure 3B, second image).  $\text{NO}_2^- \rightarrow \text{NH}_3$  should dominate the second half of the cell with a minimum HER.  $\text{NH}_3$  and leftover  $\text{NO}_2^-$  are expected to be major products. At high flow rates, the switch from  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  to  $\text{NO}_2^- \rightarrow \text{NH}_3$  should occur near the outlet due to a short  $\text{NO}_3^-$  residence time (Figure 3B, third image). A large portion of  $\text{NO}_2^-$  should remain unreacted and escape from the outlet. High  $\text{NO}_2^-/\text{NH}_3$  ratios are expected with high flow rates.

Single-pass experiments were carried out to verify our hypothesis. One advantage of single-pass operation is the consistency of catholyte composition over time. We fixed the current density at  $-200 \text{ mA cm}^{-2}$  and tested catholyte flow rates at 1, 5, 10, and 20 mL/min. Products were analyzed by ion chromatography (IC) and gas chromatography (GC). The flow diagram of the single-pass experiment can be found in Figure S3.

Product selectivity results align with our hypothesis across different flow rates in Figure 3D. At low flow rates (1 and 5 mL/min),  $\text{NH}_3$  was the dominant nitrogen product (44.3% and 61.3%  $\text{FE}_{\text{NH}_3}$ ) with nearly zero  $\text{FE}_{\text{NO}_2^-}$  (1.0% and 3.2%), while HER was

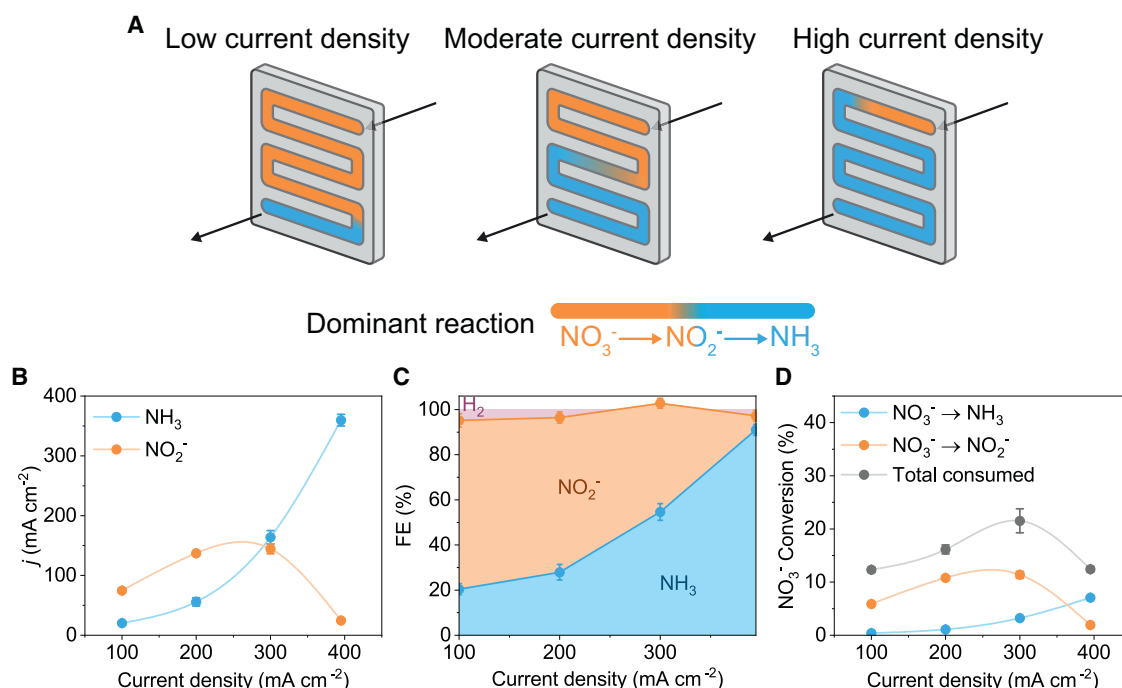
the major side reaction (Figure S5). At moderate (10 mL/min) and high (20 mL/min) flow rates, HER was suppressed to nearly zero (Figure S5).  $FE_{NO_2^-}$  increased to 65.0% with 20 mL/min, while  $FE_{NH_3}$  dropped to 32.7%. To better compare the selectivity of  $NH_3$  over  $NO_2^-$ , we calculated the ratio between  $FE_{NH_3}$  and  $FE_{NO_2^-}$  ( $FE_{NH_3}/FE_{NO_2^-}$ ) and observed a negative correlation with flow rates (Figure S6). Nitrogen mass balance was calculated to further verify the FE results (Figure S7). We found 20% of nitrogen was missing at 1 mL/min. At 1 mL/min, a high  $NH_3$  concentration accumulated during the reaction in the catholyte (>600 ppm) could lead to high diffusion from the catholyte to the anolyte or high volatilization into the air. Since  $NO_3^-$ ,  $NO_2^-$ , and  $NH_3$  were not observed in the anolyte, we suspect that the counter electrode could also oxidize  $NH_3$  to gas products (e.g.,  $N_2$ ). Under a fixed current density, partial current densities (Figure 3C) followed the same trend as FE, with the highest  $j_{NH_3} = -125 \text{ mA cm}^{-2}$  at 10 mL/min and the highest  $j_{NO_2^-} = -130 \text{ mA cm}^{-2}$  at 20 mL/min. The maximum yield of  $NH_3$  was  $10,492 \mu\text{g h}^{-1} \text{ cm}^{-2}$ , and the yield of  $NO_2^-$  was  $111,524 \mu\text{g h}^{-1} \text{ cm}^{-2}$ , as shown in Figure S8. The total conversion rate was 59% with the lowest flow rate (Figure 3E) and fell below 20% with moderate and high flow rates.

We excluded  $^{15}\text{N}$  experiments from our study due to the following reasons: (1) we obtained >1,000 ppm synthesized  $NH_3$  in the electrolyte with most conditions, which is much higher compared to potential ambient containment levels; (2) nitrogen mass balance (including leftover  $NO_3^-$ ,  $NO_2^-$ ,  $NH_3$ ) after the electrochemical reaction showed that the total measured N content at the outlet of the reactor summed to nearly 100% (generated  $NH_3 + NO_2^- +$  leftover  $NO_3^-$  vs. inputted  $NO_3^-$ ) (Figure S7); and (3) a recent study<sup>36</sup> points out the unnecessary of  $^{15}\text{N}$  experiments in  $NO_x$  electrochemical reduction to  $NH_3$  studies, which aligns with our thoughts. Thus,  $^{15}\text{N}$  isotope experiments were excluded in our study.

The full-cell potential in an MEA is a combination of cathode overpotential, anode overpotential, membrane resistance, interface resistance, Nernstian pH losses, and thermodynamic potential, plus other losses. For our flow rate study with a constant current density, we assume that the cathode overpotential dominantly affects the full-cell potential. Full-cell voltages were  $-2.8 \text{ V}$  at 1 mL/min (Figure S9), which could be due to the high HER, while with 20 mL/min, the full-cell voltages decreased to  $-2.4 \text{ V}$  with no HER.

We conducted two sets of control experiments to further prove our hypothesis. The catalytic activity of our bare carbon support (Figure S10) was examined. Bare carbon paper exhibited low  $FE_{NO_2^-}$  even with high catholyte flow rates. The results on bare carbon paper show that (1) sputtered copper is capable of promoting sequential  $NO_3^-$  conversion to  $NH_3$  via  $NO_2^-$  and (2) material with a single-step  $NO_3\text{RR}$  reaction pathway is not affected by high flow rates due to the lack of an intermediate— $NO_2^-$ . We then conducted  $NO_2^-$  electrochemical reduction with different flow rates as additional control experiments (Figure S17). We observed  $\sim 45\%$   $FE_{NH_3}$  at 1 mL/min, while  $FE_{NH_3}$  remained at  $\sim 76\%$  for 5–20 mL/min. Results at 1 mL/min indicate a  $NO_2^-$  mass transport limitation triggering a high HER. Catholyte flow rates beyond 5 mL/min can mitigate the reactant mass transport limitation.  $NO_2^-$  conversion results further confirm that the selectivity of a one-step reaction ( $NO_2^- \rightarrow NH_3$ ) is unaffected by high flow rates.

From the flow rate study, low flow rates led to a high single-pass conversion of nitrate, but considerably more unwanted HERs occurred as a result. These higher HER rates also increased the full-cell voltage. Although high flow rates resulted in



**Figure 4. Single-pass experiments at a 20 mL/min catholyte flow rate with different current densities**

(A) Schematic of hypothesized dominant reactions along the flow channel.

(B) Partial current densities of  $\text{NO}_2^-$  and  $\text{NH}_3$ .

(C) Faradaic efficiency of  $\text{NH}_3$ ,  $\text{NO}_2^-$ , and  $\text{H}_2$  where area represents FE.

(D) Conversion of  $\text{NO}_3^-$ ,  $\text{NO}_3^- \rightarrow \text{NO}_2^-$ , and  $\text{NO}_3^- \rightarrow \text{NH}_3$ .

Error bars represent the standard deviation from three replicates.

low single-pass conversion and low selectivity of  $\text{NH}_3$  over  $\text{NO}_2^-$ ,  $\text{FE}_{\text{NO}_2^-} + \text{FE}_{\text{NH}_3}$  was almost 100% with lower full-cell voltages at high flow rates, meaning that HERs can be avoided. In the next two sections, we explored two strategies possible with the MEA cell to boost the performance metrics of ammonia production: (1) boosting  $\text{FE}_{\text{NH}_3}$  over  $\text{FE}_{\text{NO}_2^-}$  using a mixture of high flow rates and varying current densities and (2) increasing the overall  $\text{NO}_3^-$  conversion rates via recirculation while maintaining high  $\text{NH}_3$  FEs.

### Maximizing ammonia production by tailoring current densities with flow rates

Our single-pass experiments at  $-200 \text{ mA cm}^{-2}$  with 20 mL/min in Figure 3 suggest that a short residence time leads to high leftover  $\text{NO}_2^-$  and that the electron supply rate at  $-200 \text{ mA cm}^{-2}$  is not fast enough to consume the remaining  $\text{NO}_2^-$ . We then hypothesized that in the MEA, we could maintain high flow rates to limit HER formation while increasing the operating current density to convert excess  $\text{NO}_2^-$  into  $\text{NH}_3$ . Thus, at 20 mL/min, higher current densities should favor  $\text{FE}_{\text{NH}_3}$  over  $\text{FE}_{\text{NO}_2^-}$ , while lower current densities should further promote  $\text{FE}_{\text{NO}_2^-}$  (Figure 4A). We then conducted further single-pass experiments with a fixed 20 mL/min catholyte flow rate and varied the current densities from  $-100$  to  $-395 \text{ mA cm}^{-2}$ .

The total FE toward  $\text{NO}_2^-$  and  $\text{NH}_3$  remained at nearly 100% with <5% FE for gas products even at  $-395 \text{ mA cm}^{-2}$ , highlighting that we can limit HER formation (Figure 4C). At 20 mL/min,  $\text{FE}_{\text{NO}_2^-}$  descended to 6% with higher current densities, while  $\text{FE}_{\text{NH}_3}$  increased and peaked at 91% at  $-395 \text{ mA cm}^{-2}$ . Full-cell voltage increased linearly with increasing current densities and reached  $-3.5 \text{ V}$  at  $-395 \text{ mA cm}^{-2}$ .

(Figure S14), which indicates substantial cell voltage from ohmic/membrane resistances. High full-cell voltages at high current densities can be reduced in the future through proper MEA design and increasing anolyte concentrations.

The highest yield of  $\text{NH}_3$  was  $30,262 \mu\text{g h}^{-1} \text{cm}^{-2}$  (Figure S11). The ratio of  $\text{FE}_{\text{NH}_3}/\text{FE}_{\text{NO}_2^-}$  showed a positive relationship with current densities at 20 mL/min (Figure S12). The partial current density for  $\text{NH}_3$  showed a non-linear relationship from  $-20$  to  $-360 \text{ mA cm}^{-2}$  (Figure 4B). Combined, these results indicate that current density can be matched with flow rate to achieve high  $\text{NH}_3$  FEs. While we could not test higher current densities due to the amperage limit of our potentiostat, we anticipate that further elevated current densities could also be achieved with higher inlet flow rates.

For nitrate conversion rates (Figure 4D), we calculated conversion percentages based on  $\text{NH}_3$  concentrations,  $\text{NO}_2^-$  concentrations, and final  $\text{NO}_3^-$  concentrations (to calculate the total consumed in Figure 4D). However, it should be pointed out that the highest  $\text{FE}_{\text{NH}_3}$  and  $j_{\text{NH}_3}$  at  $-395 \text{ mA cm}^{-2}$  did not lead to the highest  $\text{NO}_3^-$  conversion. The reason is that the  $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NH}_3$  reaction consumes 8 electrons, while  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  is a two-electron process. Moles of  $\text{NO}_3^-$  consumed can be calculated as follows:

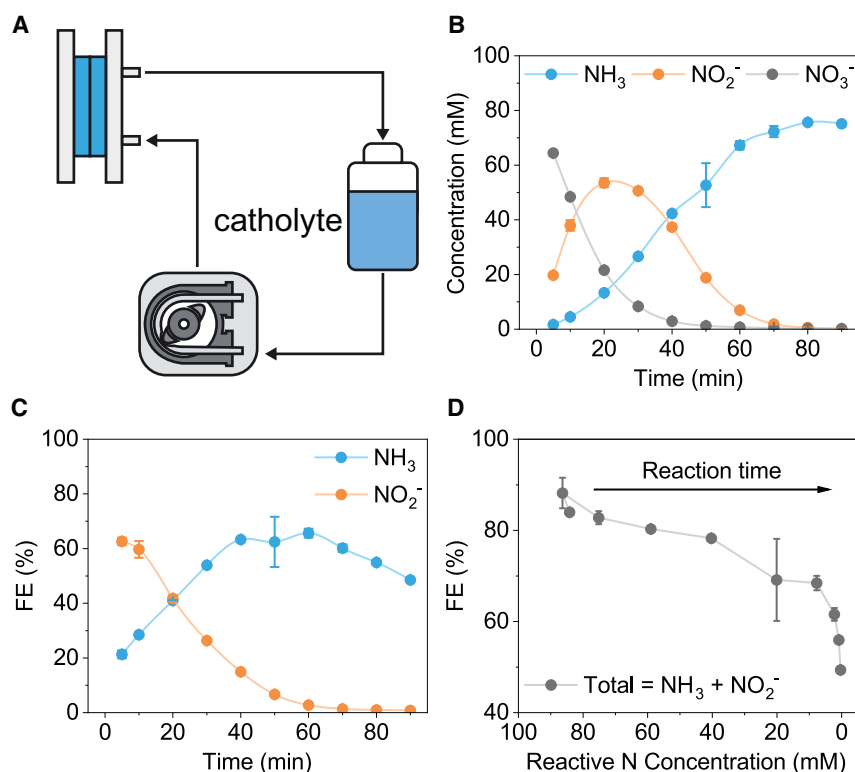
$$\text{moles of } \text{NO}_3^- \text{ consumed} = \frac{\text{total charge}}{\text{Faraday constant}} \left( \frac{\text{FE}_{\text{NH}_3}}{8} + \frac{\text{FE}_{\text{NO}_2^-}}{2} \right).$$

Thus, under the same current density and time, high  $\text{FE}_{\text{NH}_3}$  results in fewer moles of  $\text{NO}_3^-$  being consumed compared to high  $\text{FE}_{\text{NO}_2^-}$ . Nitrogen balances were calculated to verify the FE results (Figure S13), and nearly 100% of total nitrogen species were measured.

### Full $\text{NO}_3^-$ conversion via a circulation operation

In Figure 4, we demonstrated that the sequential  $\text{NO}_3^-$  conversion to  $\text{NH}_3$  is capable of achieving high FEs and current densities for ammonia through proper systematic engineering. Despite the well-controlled nature of the single-pass experiments, a key drawback of single-pass operation is the low conversion rate (<20%) at a high catholyte flow rate setting. In the next section, we explored full  $\text{NO}_3^-$  conversion through a circulation operation. To tackle the low conversion rate associated with high flow rates, we hypothesized that catholyte circulation could lead to full consumption of  $\text{NO}_3^-$  but might suffer from high HERs over time. We examined the circulation mode at  $-200 \text{ mA cm}^{-2}$  with a 50 mL catholyte circulated at 20 mL/min (Figure 5A). Liquid samples were extracted from the electrolyte reservoir every 5–10 min.

The concentration profile followed a typical sequential reaction profile (Figure 5B).  $\text{NO}_3^-$  was fully converted at 50 min via circulation mode (Figure S15B).  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  was the dominant reaction within 0–20 min, where  $\text{FE}_{\text{NO}_2^-}$  was higher than  $\text{FE}_{\text{NH}_3}$  (Figure 5C).  $\text{NO}_2^-$  as the intermediate was initially accumulated to reach a maximum concentration at 20 min and then was fully consumed (Figure 5B). The  $\text{NH}_3$  concentration profile experienced three stages, which can be identified by the slope in Figure 5B. From 0 to 20 min, the  $\text{NH}_3$  concentration increased with a small slope due to a lack of  $\text{NO}_2^-$  in the reservoir. As  $\text{NO}_2^-$  was accumulated to the maximum at 20 min, the  $\text{NH}_3$  concentration started to increase more rapidly from 20 to 60 min. The  $\text{NH}_3$  concentration reached a maximum after 60 min, when  $\text{NO}_2^-$  and  $\text{NO}_3^-$  were both fully depleted. In the circulation study, we used averaged FE to evaluate the selectivity. Averaged  $\text{FE}_{\text{NH}_3}$  began with 20% at 5 min and reached the highest at 60% from 40 to 60 min (Figure 5C). Averaged  $\text{FE}_{\text{NH}_3}$



**Figure 5. Circulation experiments result with 20 mL/min catholyte flow rate at  $-200 \text{ mA cm}^{-2}$**

(A) Schematic of circulation experiment where 50 mL catholyte was circulated at 20 mL/min.

(B) Concentration of remaining  $\text{NO}_3^-$ , synthesized  $\text{NO}_2^-$ , and synthesized  $\text{NH}_3$  in catholyte reservoir over time.

(C) Averaged  $\text{FE}_{\text{NH}_3}$  and  $\text{FE}_{\text{NO}_2^-}$  over time.

(D) Total liquid products' FE ( $\text{FE}_{\text{NH}_3} + \text{FE}_{\text{NO}_2^-}$ ) variations with reactive N concentrations (concentration $_{\text{NO}_3^-}$  + concentration $_{\text{NO}_2^-}$ ).

Error bars represent the standard deviation from three replicates.

started to drop after 60 min and as the HER dominated. The decrease in liquid FEs could be due to the mass transport limitation with the lack of reactive N compounds ( $\text{NO}_3^-$  and  $\text{NO}_2^-$ ) (Figure 5D). The full-cell voltage was over  $-3 \text{ V}$  when the HER was triggered (Figure S15A), which acts as an additional measure of how the reaction is proceeding.

For nitrogen balance, 90% of nitrogen was measured initially, while  $\sim 20\%$  of nitrogen was missing by the end of the circulation experiment. The total missing nitrogen could be attributed to reasons similar to those in the 1 mL/min single-pass experiments (Figure S7) since the concentration of  $\text{NH}_3$  reached  $>1,000 \text{ ppm}$ . We also tested the circulation mode at higher current densities, and similar trends were observed in the concentration profile and FE (Figure S16). In short, we demonstrated that electrolyte recirculation can achieve full  $\text{NO}_3^-$  conversion but suffers from high HERs as  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are consumed. Despite our promising results, future work is required to develop strategies to achieve continuous full  $\text{NO}_3^-$  conversion while maintaining high  $\text{FE}_{\text{NH}_3}$ .

## DISCUSSION

Our study explored the sequential  $\text{NO}_3^-$  reduction mechanism in an MEA. Through single-pass experiments, we identified that the residence time of reactants

determines the product selectivity and can be controlled by altering catholyte flow rates. Low flow rates offered high conversion and favored  $\text{NH}_3$  over  $\text{NO}_2^-$  but resulted in high HERs and nitrogen loss. High catholyte flow rates led to high  $\text{FE}_{\text{NH}_3} + \text{FE}_{\text{NO}_2^-}$  and low HERs but were associated with low conversion rates and low  $\text{FE}_{\text{NH}_3}/\text{FE}_{\text{NO}_2^-}$  ratios.

Copper has been previously considered a poorly performing catalyst due to its two-step sequential reaction mechanism for the  $\text{NO}_3\text{RR}$ ,<sup>23,26,28,32,33,45</sup> but we have seen near-unity ammonia FEs and current densities of  $395 \text{ mA/cm}^2$  with this simple catalyst. By balancing between the  $\text{NO}_2^-$  pool and electron supply rate, we significantly boosted the  $\text{FE}_{\text{NH}_3}/\text{FE}_{\text{NO}_2^-}$  ratio from 0.3 to 14.6 without any modification on the catalyst. Additionally, we demonstrated full  $\text{NO}_3^-$  conversion with a circulation mode and pointed out limitations such as mass transport as  $\text{NO}_3^-$  depleted over time and low average  $\text{FE}_{\text{NH}_3}$ . Further advancements in the field can now proceed through these routes.

Our investigation has shown that a two-step sequential  $\text{NO}_3^-$  reduction catalyst can benefit from the complexity of an MEA and can perform at industrial-relevant current densities. Our study represents a comprehensive examination of MEA operation parameters for sequential  $\text{NO}_3^-$  conversion. We suggest that  $\text{NO}_3\text{RR}$  design principles learned from H-cells might require tailoring when transferred into the MEA system. Designing  $\text{NO}_3\text{RR}$  catalysts in an MEA could benefit from different criteria compared to those in H-cells. For example, a segmented tandem design along the flow field could be further explored, where a  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  catalyst is fabricated near the inlet and another  $\text{NO}_2^- \rightarrow \text{NH}_3$  catalyst is located at the second half of the flow field. The insights gained from this study offer guidance when transferring previous H-cell-tested catalysts into MEA systems. In our study, we demonstrate the importance of the concentration gradient, mass transport, and residence time. We advocate that future studies should focus on transport modeling to elucidate the magnitude and potential of these parameters to alter performance, similar to efforts performed in electrochemical  $\text{CO}_2$  conversion on gas diffusion electrodes.<sup>42,46</sup>

## EXPERIMENTAL PROCEDURES

### Resource availability

#### Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Thomas Burdyny ([t.e.burdyny@tudelft.nl](mailto:t.e.burdyny@tudelft.nl)).

#### Materials availability

This study did not generate new unique materials.

#### Data and code availability

The data presented in this work are available from the corresponding author upon reasonable request.

### Materials

Cathodes were prepared through direct-current magnetron sputtering copper (Cu) at a pressure of  $3 \mu\text{bar}$  onto a carbon gas diffusion layer (Sigracet 39 AA, Fuel Cell Store). The thickness of the Cu layer was controlled by adjusting the power supply and sputtering time. Prepared cathodes were stored in a glovebox with an inert atmosphere to minimize oxidation. The cell structure illustration is presented in [Figure 2A](#). Nickel foam (Recemat BV) was used as the anode. Nafion 115 (Ion Power) was pretreated in 1 M KOH prior to experiments and used as the cation exchange

membrane. A 5.06 cm<sup>2</sup> (2.25 × 2.25 cm) electrolyzer was used in this study, where flow fields for the cathode and the anode are serpentine type and pin type, respectively. 1 M KOH + 0.1 M KNO<sub>3</sub> was prepared (KNO<sub>3</sub> 99% Alfa Aesar) and used as the catholyte. 1 M KOH was used as the anolyte.

## Methods

Flow rates of catholyte and anolyte were controlled by two separate peristaltic pumps (Figure S3). It should be noted that the anolyte was circulated for all experiments. For our two-electrode MEA, the current input was controlled by an electrochemical testing station, and the cell voltage was measured as the response. Cathode liquid samples were collected using a syringe and analyzed by two separate ICs (one for measuring NO<sub>2</sub><sup>−</sup> and NO<sub>3</sub><sup>−</sup> and one for measuring NH<sub>4</sub><sup>+</sup>) (Metrohm). Argon was purged into catholyte headspace, and gas samples were measured by an auto-GC (Global Analyser Solutions).

## SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2024.101977>.

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## AUTHOR CONTRIBUTIONS

T.Y. and T.B. conceived the project. T.Y. led experiments, data analysis, and figure design. Min Li assisted with electrochemical testing, IC measurements, and scientific discussion. S.S. and J.K. performed catalyst fabrication and assisted with GC measurements. Mengran Li assisted with electrochemical testing, data analysis, and scientific discussion. A.U. assisted with scientific discussion and equipment. O.V. and T.B. assisted with project supervision, scientific discussion, and funding. T.Y. and T.B. wrote the manuscript with editing contributions from all the authors.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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