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Non-aqueous gas diffusion electrodes for rapid ammonia synthesis from nitrogen and water-splitting-derived hydrogen

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Supplementary Methods

The procedures and materials for nitrogen reduction outlined below have been optimized for reliable ammonia production. However, certain deviations from the procedure and material vendors, which are specifically called out in-text and in prior work,¹ may lead to poorer ammonia production. We recommend closely following the procedure for reproducibility and high yields.

Materials

Tetrahydrofuran (THF, 99+%, stabilized with BHT) and molecular sieves (3Å, 4-8 mesh) were purchased from Acros Organics. Lithium tetrafluoroborate (LiBF₄, 98%), dimethyl carbonate (DMC, ReagentPlus, 99%), propylene carbonate (PC, anhydrous, 99.7%), maleic acid (ReagentPlus, ≥99%), sodium salicylate (ReagentPlus®, ≥99.5%), sodium hypochlorite (NaOCl, 10-15%), nickel chloride hexahydrate (NiCl₂·6H₂O), hydrochloric acid (HCl, 37%), and ferrocenium hexafluorophosphate (FcPF₆, 97%) were purchased from Sigma-Aldrich. Hexanes (C₆H₁₄), diethyl ether (Et₂O), and sulfuric acid (H₂SO₄, 93-98%, trace metal grade) were purchased from Fisher Scientific. Platinum foil (Pt, 0.025 mm thick, 99.99%, trace metals basis) and sodium citrate (anhydrous) were purchased from Beantown Chemical. Ethyl alcohol (C₂H₅OH, Koptec, anhydrous, 200 proof), sodium hydroxide (NaOH, Macron Fine Chemicals, pellet form), and acetone (ACS, BDH Chemical) were purchased from VWR International. Sodium nitroprusside (99-102%), ferrocene (Fc, 99%, powder), boric acid (H₃BO₃, 99.99%, trace metals grade), nickel foil (annealed, 99+%, 0.05 mm), ammonium chloride (NH₄Cl, anhydrous, 99.99%), and ammonium hexachloroplatinate (IV) ((NH₄)₂PtCl₆, 43.4% min Pt) were purchased from Alfa Aesar. Isotope labelled nitrogen (¹⁵N₂, 98%+) was purchased from Cambridge Isotope Laboratories, Inc. Argon gas (UHP, 5.0 grade) and hydrogen gas (UHP, 5.0 grade) were purchased from Airgas. Nitrogen gas was available in-house; it is generated by boil-off of liquid nitrogen from Airgas. Milli-Q water was obtained by filtering deionized (DI) water through a Milli-Q purification system (Merck, Millipore Corporation). Steel cloth (304 stainless steel, 400x400 mesh) and steel foil (cold-worked 304 stainless steel, 0.002" thick) were purchased from McMaster-Carr. Platinum-coated carbon paper (0.5 mg cm⁻² 60% platinum on Vulcan, carbon paper) was purchased from FuelCellStore. Polyporous Daramic 175 separators were received as a sample from Daramic (Charlotte, NC).

Electrolyte solution preparation

Dry THF was used as the solvent in THF-based experiments described below. It was obtained by drying as-purchased THF over 20% v/v of freshly dried molecular sieves for at least 48 hours in a round-bottom flask sealed with a rubber septum stopper. The sieves were prepared by washing with acetone and heating at 300 °C for 5 hours in a muffle furnace. The water content of dry THF was found to be 7.1±0.3 ppm (n = 3) via Karl-Fischer titration. As-purchased LiBF₄, stored in an Ar glovebox, was dissolved in dry THF to obtain electrolyte solutions containing 1 M LiBF₄. As discussed in previous work,¹ it is imperative for the LiBF₄ to be pure; LiBF₄ purchased from Sigma-Aldrich was found to be sufficiently pure for these experiments, while other vendors' may require purification. Ethanol was added to the solution to obtain a concentration of EtOH of 0.11 M. Insoluble residue was removed from the solutions by centrifugation at 6000 rpm (4430 ref) for 10 minutes. Clear electrolyte solutions were stored in oven-dried glass vials in a desiccator and used within 12 hours of preparation. While the solutions are somewhat water sensitive,¹ we

found that performing centrifugation and solution transfer operations in atmospheric air is permissible, as long as the operations do not expose the solutions to air for long periods of time (hours, e.g. during storage). Oxygen from the atmosphere is typically purged from the electrolyte during saturation by gas flow (see below).

In propylene carbonate-based experiments, solvents and the electrolyte salt were used as received. LiBF_4 was dissolved in a 9:1 by volume mixture of propylene carbonate and dimethyl carbonate to produce a 1 M LiBF_4 in PC/DMC electrolyte. Dimethyl carbonate was added to the electrolyte in order to reduce the viscosity of the solution, as opposed to using pure propylene carbonate as the solvent. The resulting solution was centrifuged at 6000 rpm (4430 rcf) for 20 minutes to remove insoluble impurities. Clear electrolyte was transferred to oven-dried vials and used within 12 hours of preparation.

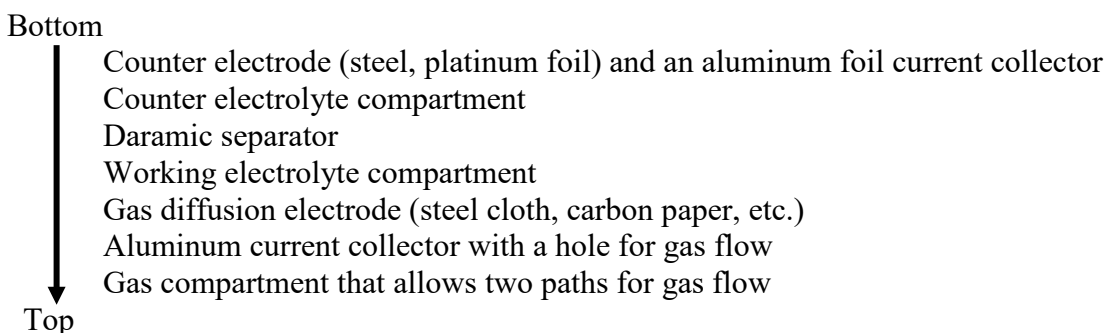
Nitrogen reduction experiments – steel foils

Flooded steel foil experiments (Fig. 1c) were performed analogously to copper foil experiments described in previous work.¹ Briefly, two-compartment cells were assembled with a steel foil cathode, platinum foil anode, and a Daramic separator. Steel foils were prepared by polishing with 400 grit sandpaper, followed by 1500 grit sandpaper, and finally by rinsing with DI water and drying in air at 80 °C. Daramic separators were prepared by successively soaking them in THF and water several times, as follows: as-received separators were immersed in as-purchased THF for ~10 minutes with agitation, after which the solution turned yellow. The separators were then immersed in water for ~10 minutes to remove THF and water-soluble impurities. The process of immersing in fresh THF and water was repeated two more times, after which the separators were dried in air at 80 °C. On rare occasions, fresh Daramic separators may initially lead to poor ammonia yields, likely due to contaminants left in the porous structure. Ammonia yields reach steady values after reusing the separator twice or more. All cell parts, separators, and electrodes were washed with DI water and dried in an oven at 80 °C prior to use. Daramic separators are also soaked in DI water for at least 10 minutes to remove electrolyte and residual ammonia from the structure prior to drying. We recommend rinsing the cell parts with THF, acetone, and water if cell parts are new or have been previously used for other chemistries to remove impurities that may affect yields. Cell parts, separators, and platinum foils are reused multiple times, while the steel foils are used in only one experiment before being discarded. 1.75 mL of 1 M LiBF_4 , 0.11 M EtOH in THF electrolyte was added to each compartment of the cell. Note that this is the volume of electrolyte added to each compartment and may not be the final electrolyte volume due to electrolyte evaporation. THF-saturated N_2 gas was bubbled through the cathode compartment at 10 standard cubic centimeters per minute (sccm) for 10 minutes to saturate the solution with N_2 . A chosen constant current was then supplied to the cell using a Biologic VMP3 potentiostat, Tekpower TP3005T, or Tekpower TP5003T DC power supply. When using a power supply, the current was monitored by measuring the potential drop across a calibrated 33-Ohm resistor in series with the electrochemical cell (Supplementary Fig. 23). Approximately 7.2 coulombs of charge were supplied in each experiment. The catholyte was removed from the cell and diluted with Milli-Q water in a 50 mL volumetric flask. The cathode compartment was rinsed twice with Milli-Q water and added to the flask, after which the solution was diluted to the mark. Three samples for ammonia quantification were made: one containing only 2000 μL of the diluted catholyte, one containing 1000 μL of the diluted catholyte and 1000 μL of Milli-Q water, and one containing 500 μL of the diluted catholyte and 1500 μL of Milli-Q water.

Assembly of gas diffusion cell

Gas diffusion experiments were performed using 3- and 4-compartment cells (Supplementary Fig. 15, Fig. 4d). In a 3-compartment cell, there are gas, working, and counter compartments, the latter two separated by a piece of Daramic. Daramic separators were prepared by washing in THF and water, as described above in *Nitrogen reduction experiments – steel foils*.

All cell parts, separators, and electrodes were dried in an oven at 80 °C prior to use. Aluminum current collectors for the GDE were made from 0.016” thick 6061 aluminum; the hole was made with a 7/16” wood drill bit and sanded to smooth the edges. O-rings between the compartments (Supplementary Figs. 15 and 16) are important for making a good gas seal. We recommend using fluoropolymer-coated silicon O-rings, as they are compatible with THF. The procedure to assemble a cell can be seen in Supplementary Fig. 16. In words, a “stack” is made by placing the pieces in the following order:

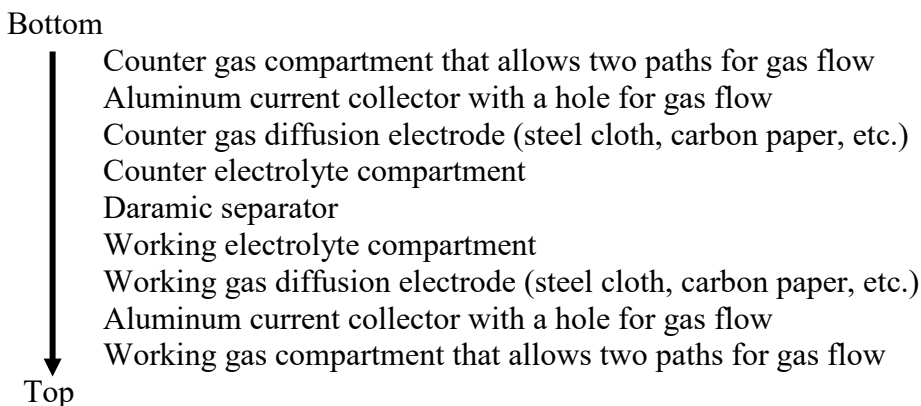


Once the cell is assembled, the inlet of the gas compartment is attached to a bubbler containing THF, through which the gas is bubbled. The outlet is attached to a tube that enters a tall (50 cm) burette containing a water column to control the gauge pressure inside the gas compartment and the pressure gradient across the GDE (Supplementary Fig. 17); in NRR experiments, a 0.1 M H_3BO_3 in Milli-Q acid trap is inserted between the outlet of the cell and the burette (Supplementary Fig. 17) to capture gas phase ammonia.

After the cell is set up and gas is flowing through the bubbler at 10 sccm, 1.75 mL of $\text{LiBF}_4/\text{EtOH}/\text{THF}$ electrolyte are added to the counter compartment, followed by 1.75 mL of electrolyte to the working compartment. Note that this is the volume of electrolyte added to each compartment and may not be the final electrolyte volume due to electrolyte evaporation. Initially, some of the electrolyte in the working compartment may enter the gas compartment; however, after the entire GDE is contacted by the electrolyte, the pressure in the gas compartment increases, as evidenced by motion of the gas level in the burette, and the electrolyte returns to the working compartment, after which gas begins to flow through the GDE (Supplementary Fig. 2). When using bare steel cloths, the pressure in the gas compartment during gas flow through the GDE is typically 1.6-1.8 kPag, corresponding to 16-18 centimeters of water column above the gas. The pressure in a flow through configuration is 1.8-2.0 kPag when platinum-coated steel cloths are used. The working compartment electrolyte is saturated with the fed gas by flowing it through the GDE for 10 minutes. Following saturation, the water level in the burette is decreased to lower the pressure in the gas compartment to the desired value and favor gas flow past the GDE and out of the gas compartment (Supplementary Fig. 17). Some gas bubbles begin to flow out into the burette almost immediately upon lowering of the pressure in the gas compartment below the flow-through pressure. The addition of an acid trap in NRR experiments (Supplementary Fig. 17) adds

approximately 2 cm of water of additional gauge pressure in the gas compartment, which is accounted for when computing pressure gradients across the GDE. At this point, the flowrate of the gas can be reduced if desired, such as in experiments where the effect of flowrate past the electrode is quantified, after which current is applied. The electrolyte in the working compartment was removed and analyzed after application of current.

In a 4-compartment cell used in combined electrochemical Haber-Bosch (eHB) experiments, the setup is similar to the aforementioned 3-compartment cell. The main change is that the counter electrode is replaced by a second gas compartment and gas diffusion electrode. In summary, the stack becomes:



Nitrogen reduction experiments – steel cloth experiments

Nitrogen reduction reaction (NRR) experiments focused on studying the NRR on steel cloths were performed in 3-compartment cells, the setup of which is detailed in *Assembly of a gas diffusion cell*. A platinum foil anode and a circular stainless steel cloth (SSC) cathode (diameter = 14 mm) were used as the electrodes. The steel cloth electrode was rinsed with DI water and dried at 80 °C prior to use; it was used only for one experiment before discarding. The platinum foil was reused indefinitely. The method of applying current and preparing quantification samples was analogous to the method described in *Nitrogen reduction experiments - steel foil experiments*, with one change: the catholyte was diluted in a 100 mL volumetric flask due to higher amounts of produced NH_3 .

One modification that was made in NRR experiments was the addition of a 2 mL 0.1 M boric acid trap between the gas compartment and the pressure-controlling burette to capture any gas phase ammonia. In experiments where gas was fed through the SSC, the trap was inserted at the gas outlet in the catholyte chamber, so all fed gas still went through it. When no pressure gradient across the SSC was applied (Fig. 3d), no boric acid trap was present, hence no quantification of gas phase products could be performed. While this may have underestimated the amount of ammonia produced, it is likely that little ammonia was found in the gas phase in this experiment, as ammonia stripping from bulk solution in the gas compartment likely does not occur (Supplementary Figs. 2 and 24). After each experiment, the solution in the trap was quenched with 500 μL of 0.4 M NaOH and diluted in a 25 mL volumetric flask with Milli-Q water, after which the ammonia concentration in the solution was quantified.

Nitrogen reduction experiments – time evolution of ammonia

We performed experiments in which the concentration of ammonia in the electrolyte was measured as a function of operating time (Supplementary Fig. 13). In these experiments, the setup was analogous to the experiments described in *Nitrogen reduction experiments – steel cloth experiments*, except that 1.9 mL of electrolyte were added to the cathode compartment instead of the usual 1.75 mL, providing extra electrolyte for periodically removing aliquots. A 20 mA cm⁻² current was applied for 10 minutes in these experiments to maintain a high production rate while allowing for good temporal resolution of the data. 10 sccm of THF-saturated N₂ were flowed through the SSC to allow for bulk mixing in the electrolyte. Every 60 seconds, nominally 20 µL of catholyte were extracted from the cathode compartment via pipette. Because the electrolyte forms a thin film on the inside of the pipette tips that cannot readily be utilized, precise quantification of the amount withdrawn is difficult. By measuring the mass of electrolyte that can be recovered from the tips (not during the experiment), we found that approximately 16 µL of electrolyte were used to make quantification samples. The extracted catholyte was diluted in 2 mL of Milli-Q water. The ammonia content of the two samples was quantified as described below. The amount of ammonia produced at each time point (Supplementary Fig. 13) was computed according to Supplementary Equation 1, in which $V_{extract}$ is the volume of the catholyte extracted (20 µL), and t_n is the number of minutes elapsed since the beginning of the experiment.

$$n_{NH_3}(t) = (V_0 - V_{extract} \cdot t_n) \cdot C(t) \quad (1)$$

After the experiment, the cathode was diluted in a 100 mL volumetric flask to quantify the remaining ammonia.

Ammonia quantification – calibration solution preparation

A fresh calibration curve was made during each batch of quantifications. The calibration solutions contained a known amount of NH₄Cl in Milli-Q water (Supplementary Fig. 19). While ammonia samples from NRR experiments had some amount of LiBF₄, EtOH, and THF in them, they were sufficiently dilute as to not affect the quantification significantly (Supplementary Fig. 19). The absorbance of solutions containing THF is diminished, potentially leading to an underestimate in ammonia concentration, as pure water calibrations curves (Supplementary Fig. 19) were used for all analyses.

¹⁵N₂ isotope labeling experiments

Isotope labeling experiments were used as a control to confirm N₂ reduction to NH₃. In order to remove any NH₃ and NO_x potentially found in ¹⁵N₂ stock (and house ¹⁴N₂), the gases were successively passed through solutions of 0.1 M NaOH in water (to capture NO_x), 0.05 M H₂SO₄ in water (to capture NH₃), and THF containing activated molecular sieves (to capture water and to saturate the gas with THF) before being fed to the cell. Two isotope labeling experiments were performed: one utilized a typical 3-compartment cells with a steel cloth cathode, Daramic separator, and platinum foil anode with pressure control, while the other utilized an eHB reactor with a steel cloth cathode, Pt/SSC anode, and no separator.

Prior to any experiments, 10 sccm of Ar were bubbled through the entire setup (traps, bubbler, and cell) for 15 minutes to remove trace amounts of ¹⁴N₂ and other impurities. The desired gas (Ar, ¹⁴N₂, or ¹⁵N₂) was fed to the cell and through the SSC at 5 sccm for 10 minutes. In the eHB experiment, H₂ was fed through the Pt/SSC at 5 sccm for 10 minutes as well.

In the 3-compartment cell experiment, the pressure gradient across the SSC was decreased to 1 kPa, after which 25 mA of current were applied for 4.8 minutes. The catholyte was removed

from the cell into a glass vial. The cathode compartment was rinsed with 0.05 M H_2SO_4 twice and the resulting fractions were added to the catholyte. The entire mixture was diluted to ~4 mL with 0.05 M H_2SO_4 . Similarly, the boric acid trap was diluted to a total volume of ~4 mL with 0.05 M H_2SO_4 . The solution was acidified to convert all the ammonia to ammonium (NH_4^+) for NMR analysis.²

In the eHB experiment, the pressure gradient across both electrodes was decreased to 1 kPa, after which the gases were flowed past the electrodes for an additional 2 minutes. 20 mA of current were passed for 6 minutes. The electrolyte was removed from the cell into a 10 mL volumetric flask. The cell was rinsed with 0.05 M H_2SO_4 and the resulting solutions were added to the volumetric flask and diluted to the mark (10 mL). The boric acid trap was diluted to a total volume of ~4 mL with 0.05 M H_2SO_4 .

The ammonia content in the resulting solutions was quantified using the salicylate method described in the Methods section of the main text. The electrolyte solutions for quantification were neutralized and diluted 50-fold (40 μL of sample, 10 μL of 0.4 M NaOH, 1950 μL of water) in 3 compartment case or 20-fold (100 μL of sample, 25 μL of 0.4 M NaOH, 1875 μL of water) in the eHB case, while the trap solutions were diluted 10-fold (200 μL of sample, 50 μL of 0.4 M NaOH, 1750 μL of water). NMR spectra of the undiluted solutions were measured on a three-channel Bruker Avance Neo 500.18 MHz spectrometer. Solvent suppression of the largest one (H_2O) or three ($\text{THF}+\text{H}_2\text{O}$) peaks was used to increase the signal-to-noise ratio for ammonium peaks. Locking and shimming was done on ^1H from water in the solution; no additional compounds were added to the solution prior to NMR. 64 scans were measured for all spectra. The N-H coupling in the NMR spectra confirms ammonia formation from feed N_2 (Extended Data Fig. 2c).

Preparation of platinum-coated steel cloths

In order to prepare an SSC for hydrogen oxidation, platinum metal, an effective HOR catalyst, was electrodeposited onto the steel cloths. We found that platinum metal has poor adhesion to stainless steel, which has also been observed in the literature.³ In view of this, the steel cloths were first treated by “striking” with nickel. A Wood’s nickel strike solution, which consists of 1 M NiCl_2 and 1 M HCl in water, was used. Typically, a piece of steel cloth that is 3 cm by 5 cm is taken and submerged to have 2.5 cm by 5 cm in the nickel strike solution. The cloth was used as the working electrode while a piece of nickel foil was used as the soluble counter electrode in an undivided beaker cell. The cloth was pretreated by applying an oxidative current of 15 mA $\text{cm}_{\text{geom}}^{-2}$ for 30 seconds, immediately after which a reductive current of 30 mA $\text{cm}_{\text{geom}}^{-2}$ was applied for 5 minutes obtain a nickel-plated stainless steel cloth. The cloth was thoroughly rinsed with DI water and dried in air at 80 °C. The cell potential required for nickel plating was typically ~1 V. Some of the current went toward hydrogen evolution, evidenced by gas evolution on the cloth; assuming 90% FE toward nickel plating, the resulting nickel layer is approximately 3 μm thick. The cloths visibly change colors after striking with nickel (Supplementary Fig. 3).

After striking the cloth with nickel, platinum can be deposited. The nickel-stricken cloth was cut into smaller pieces to submerge ~1.5 cm by 1.5 cm into 10 mL of a platinum plating solution. The platinum plating solution used was a citrate-ammonium bath, chosen for its high current efficiency toward platinum plating, low current density required, and the non-hygroscopic nature of the platinum precursor.^{4,5} The bath contained 35 mM $(\text{NH}_4)_2\text{PtCl}_6$, 400 mM trisodium citrate, and 75 mM of NH_4Cl . The nickel-stricken cloth is used as the working electrode; a piece of platinum foil is used as a soluble counter electrode in a beaker cell, which is kept over a water bath at 90 °C. It is possible that the $(\text{NH}_4)_2\text{PtCl}_6$ will not fully dissolve until the solution reaches

90 °C. A constant reductive current of 10 mA ($\sim 5 \text{ mA cm}_{\text{geom}}^{-2}$) was applied to the cloth for 5 minutes. The cell potential required for platinum plating is typically ~ 1.7 - 1.8 V. If the potential was lower than ~ 1.7 V, then a higher current, up to 20 mA, was applied; this is common for fresh baths. The cloth should turn darker after platinum plating (Supplementary Fig. 3). The cloth was thoroughly rinsed with DI water and dried at 80 °C. A 14 mm diameter circle was cut out to be used as the HOR electrode, and was typically used in only one experiment prior to being discarded. The entire platinum deposition procedure is unoptimized and may require further improvement for practical applications.

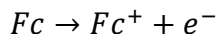
Ammonia contamination in the cathode compartment from the Pt/SSC anode is unlikely as using Pt foils (in 3-compartment experiments as opposed to Pt/SSC in 4-compartment and undivided experiments) which have not been in contact with the ammonium bath as the anode also leads to production of ammonia in NRR experiments (Fig. 4b). Ar and isotope labeling experiments confirm ammonia production via nitrogen reduction (Extended Data Fig. 2).

Hydrogen oxidation experiments

Hydrogen oxidation experiments focused on studying HOR were performed in 3-compartment cells, the setup of which is detailed in *Assembly of a gas diffusion cell*. The cell parts and separators were washed with acetone (to remove residual ferrocene) and water and dried in an oven at 80 °C between experiments. A steel foil was used as the cathode, while Pt-coated steel cloths or Pt/C carbon paper disks were used as the anode; both the anode and cathode materials were fresh in every experiment and used only once. 10 sccm of H₂ were flowed past the anode after saturating the electrolyte with H₂. Regardless of current applied, 7.2 coulombs of charge were passed through the cell, after which hydrogen oxidation Faradaic efficiency was quantified as described below in *Quantification of hydrogen oxidation*. In certain experiments (Fig. 3b), no pressure control in the gas compartment was used: the hydrogen gas was vented directly to a continuously operating fume hood. Some control experiments were performed where N₂ gas was fed instead of H₂ gas to the anode; the HOR FE was found to be zero to within error (Supplementary Fig. 21).

Quantification of hydrogen oxidation via ferrocene oxidation

The Faradaic efficiency for hydrogen oxidation was quantified indirectly by observing the competing ferrocene oxidation reaction:



As ferrocene is thermodynamically more difficult to oxidize than H₂ but is easier to oxidize than THF (Fig. 1b, Supplementary Fig. 25),⁶ any applied current would first oxidize H₂ to solvated protons, assuming the oxidation is kinetically facile, and then ferrocene to ferrocenium, once HOR is diffusion limited. In theory, ferrocene is easier to oxidize than its equilibrium potential suggests (Supplementary Fig. 25) due to a Nernstian concentration correction, as little ferrocenium is present in the original solution. In practice, however, the error associated with the concentration correction is quite small, as even a 400 mV shift in the oxidation potential requires only 54 nM of ferrocenium to be present in the electrolyte with 250 mM of ferrocene. This implies the vast majority of ferrocenium is formed via ferrocene oxidation during application of a current when hydrogen oxidation is not occurring. Solvent oxidation is avoided by having a large concentration of ferrocene, which increases the transport limited ferrocene oxidation current density, and prevents significant depletion of ferrocene during the course of the experiment.

Ferrocene was dissolved in the electrolyte containing 1 M LiBF₄, 0.11 M EtOH in THF immediately before the runs to obtain a ferrocene concentration of 250 mM (typically by adding 186 mg of ferrocene to 4 mL of electrolyte). Hydrogen oxidation was performed as described in *Hydrogen oxidation experiments*, after which the anolyte was removed into a centrifuge tube and the anode compartment was washed with N₂-purged Milli-Q water twice. The water was purged with N₂ to remove O₂, which could contribute to ferrocene oxidation or ferrocenium decomposition.⁷ Upon addition of water, any unreacted ferrocene precipitates out, while ferrocenium remains in solution. The THF/water mixture was diluted to ~10 mL with N₂-purged water. The cloudy solution was extracted with ~3 mL of N₂-purged hexanes three times to dissolve and extract ferrocene from the aqueous phase. We found that THF is also extracted into the organic phase. The aqueous solution was diluted to 10 mL with N₂-purged water and centrifuged to promote phase separation of residual hexanes. The concentration of ferrocenium in the obtained aqueous solution was quantified by UV-vis in quartz glass cuvettes (Supplementary Fig. 21). The absorbance signal was computed similar to the way it is computed for ammonia quantification: the difference between peak absorbance and absorbance at another arbitrary wavelength. At high concentrations of ferrocenium, the visible peak at 619 nm was used for quantification. At low concentrations, the significantly more absorbing UV peak at 255 nm was used. The absorbance minimum at 438 nm was used as the reference absorbance for subtraction.

As-purchased FcPF₆ was purified to obtain a more accurate calibration curve for ferrocenium. FcPF₆ was dissolved in acetone to obtain a concentrated solution. The solution was centrifuged twice to remove brown insoluble impurities. Diethyl ether was then added to the solution to precipitate out the FcPF₆. The solution was cooled to -20 °C, after which the solids were collected and washed with diethyl ether. After drying under vacuum, a blue powder of purified FcPF₆ was obtained.

The exact extinction coefficient for ferrocenium was difficult to establish (Supplementary Fig. 21). For one calibration curve, 20 mg of purified FcPF₆ was dissolved in 10 mL of N₂-purged Milli-Q water. The solution was centrifuged to remove small amounts of undissolved impurities, likely ferrocene or iron oxide, after which the stock was used to make a calibration curve. For other calibration curves, 20 mg of purified FcPF₆ and 90 mg of ferrocene were dissolved in 2 mL of either 1 M LiBF₄/THF or 1 M LiBF₄/0.11 M EtOH/THF, both purged with N₂; these solutions are meant to simulate the electrolyte after an HOR experiment. The solutions were then prepared similarly to the way samples were prepared in HOR experiments: by diluting with water, extracting the ferrocene with hexanes, and centrifuging for phase separation. The obtained aqueous stocks were used to make calibration curves. We found it difficult to reliably obtain an extinction coefficient under different solution preparation conditions (Supplementary Fig. 21), and therefore chose extinction coefficients based on experimental observations. We chose an extinction coefficient of $135 \pm 20 \text{ M}^{-1} \text{ cm}^{-1}$ for the 619 nm signal and $7100 \pm 1400 \text{ M}^{-1} \text{ cm}^{-1}$ for the 255 nm signal; these are the averages of the extinction coefficients obtained by various methods. This choice of extinction coefficient also gives an HOR FE of zero within error when N₂ is fed to a Pt/SSC anode (Supplementary Fig. 21).

As some small amount ferrocenium may be present in the stock ferrocene or in the solution from oxidation by trace oxygen, we performed control experiments where no current was applied (Supplementary Fig. 21). Typical HOR 3-compartment cells were built with Pt/SSC anodes, and H₂ was fed through the cell for 10 minutes. H₂ was then flowed past the GDE at a 1 kPa gradient across the GDE for 5 or 15 minutes. Ferrocenium was extracted into an aqueous phase and was

quantified as described above; the concentration was found to be $C_0 = 34 \pm 12 \text{ } \mu\text{M}$ in the final 10 mL of aqueous solution.

The final formula used to estimate FE of HOR is presented as Supplementary Equation 2.

$$FE_{HOR} = 1 - \frac{F \cdot V_{sol}}{I \cdot t} \cdot \left(\max \left(\frac{A_{619} - A_{438}}{\epsilon_{S,619}}, \frac{A_{255} - A_{438}}{\epsilon_{S,255}} \right) - C_0 \right) \quad (2)$$

FEs that were computed to be negative were assumed to be zero.

We feel it is important to note that this experiment was designed to accurately measure small deviations from unity FE for hydrogen oxidation, as we are primarily interested in oxidizing hydrogen with nearly unity FE. When little ferrocene is oxidized, we are very confident that H_2 is getting oxidized. When a large amount of ferrocene is oxidized, we can infer that hydrogen oxidation is poor, but the exact value may have a larger uncertainty, as can be seen for HOR FE at Pt/C electrodes (Fig. 3a). However, we can tolerate a large uncertainty at low HOR FEs as the electrodes that operate in that regime are undesired to begin with. Other methods to quantify FE such as gas chromatography analysis or mass balancing either have uniform error bars across the entire FE range, or have low error bars when the FE is low (i.e. have a high confidence in a null signal).

Quantification of hydrogen oxidation via mass balance

In cases where the flowrate of gas past GDEs is low and the applied current is high, the conversion of the gas may be high (Supplementary Fig. 10). The nominal conversion ξ in this case is defined in Supplementary Equation 3.

$$\xi = \frac{I_{applied} \cdot FE}{nF \cdot Q_{applied} \cdot \frac{P_0}{RT_0}} \quad (3)$$

In Supplementary Equation 3, $I_{applied}$ is the applied current density, FE is the Faradaic efficiency towards the reaction of interest, n is the number of electrons involved in the electrochemical reaction ($n = 2$ for HOR, $n = 6$ for NRR), F is Faraday's constant, $Q_{applied}$ is the flowrate of gas set using the flow controller, R is the universal gas constant, T_0 and P_0 are the standard temperature and pressure (273K, 1 bar), respectively, used if the $Q_{applied}$ is given in units standard volumetric flow units (e.g. sccm).

The conversion can be estimated by measuring the outlet flowrate of gas and by using a mass balance over the gas in the gas compartment, given in Supplementary Equation 4.

$$Q_{in} - Q_{out} = \xi Q_{in} \quad (4)$$

From Supplementary Equations 3 and 4, the Faradaic efficiency of gas conversion can be computed. Implicitly, we are assuming that the gas compartment does not have leaks, and that gas dissolution into the electrolyte is negligible. Practically, this process may be used to quantify hydrogen oxidation, as the conversions can be very high.

The flowrate of gas leaving the compartment is difficult to quantify using a flow controller as it is directed to a pressure-controlling water column which releases the gas to the ambient environment and adds additional back pressure which may be difficult to control (Supplementary Fig. 17). Therefore, to quantify the flowrate of gas leaving the gas compartment, the time between bubbles of gas detaching the tubing in the water column (Supplementary Fig. 17) was measured by an electronic stopwatch. This method assumes that the volume of gas bubbles is fairly constant and independent of flowrate, i.e. that they only detach when they reach a critical volume. The critical bubble volume was found to change with tubing orientation and gas, and so only results in the same set can be compared directly. The bubble size can be "calibrated" by measuring the

interval between bubble detachments at a given flowrate when no current is applied. Thus, the outlet flowrate was computed using Supplementary Equation 5.

$$Q_{out} = \frac{Q_{nominal\ in} \cdot t_{no\ current}}{t_{with\ current}} \quad (5)$$

The HOR FE quantification experiments were performed using 3-compartment cells with a Pt/SSC anode, Daramic separator, and steel cathode. The electrolyte used was either 1 M LiBF₄/0.11 M EtOH/THF (Supplementary Fig. 9) or 1 M LiBF₄ in 9:1 PC/DMC (Supplementary Fig. 11). First, the average time for bubble detachment was measured when flowing 0.5 sccm of the desired gas (N₂ for controls and H₂ for HOR quantification) without applying current. Then, 25 mA of current were applied without changing tubing configuration or flowrate, and the average time for bubble detachment was recorded.

We found that when N₂ is fed to the cell, the interval between bubbles does not significantly change for either tested electrolyte when current is applied (Supplementary Figs. 9 and 11), while the interval increases when H₂ is fed and current is applied (Supplementary Figs. 9 and 11). The Faradaic efficiency for HOR can be estimated from these data; it was found to be 105±2% for oxidation using THF-based electrolyte (Supplementary Fig. 9) and 112±19% for PC-based electrolyte (Supplementary Fig. 11).

A limitation with the method of mass balancing was found, however. When hydrogen is fed at a rate of 0.2 sccm to a 3-compartment cell with a Pt/SSC anode and THF-based electrolyte and 25 mA of current are applied, there should be some gas leaving the gas compartment, as 25 mA corresponds to a hydrogen oxidation rate of at most 0.176 sccm at 100% FE. However, we observe that no bubbles are evolved and the level of the total amount of gas decreases with time; a constant amount of gas with 25 mA of applied current is obtained when H₂ is fed at a rate of 0.22-0.23 sccm. While this demonstrates the limitation of the mass balance method and possible unaccounted for sources of hydrogen depletion, we can confidently say that hydrogen is oxidized at high rates in this system with close to unity FE.

eHB experiments and coupling to water splitting

A 4-compartment cell with a steel cloth cathode and Pt/SSC anode was assembled as described in *Assembly of a gas diffusion cell*. The operation of the 4-compartment cell was similar to operation of the 3-compartment cells in NRR and HOR experiments. 3.5 mL of 1 M LiBF₄, 0.11 M EtOH in THF were added to the 4-compartment cell (1.75 mL to each compartment), while 10 sccm of THF-rich N₂ and 10 sccm of THF-rich H₂ were fed to the cathode and anode compartments, respectively. The solutions were saturated with their respective gases for 10 minutes by flowing gas through the SSCs. The pressure gradient across the SSCs was lowered using a water column to 1 kPa, at which point the gas flowed past the SSC. 25 mA were applied to the cell for 4.8 minutes, after which the ammonia content of the cathode chamber was analyzed as described in *Nitrogen reduction experiments*.

In long term experiments (Fig. 4b), 20 mA were applied for 1 hour in a 3-compartment cell with a platinum foil anode or 1-2 hours in a 4-compartment eHB cell. Photographs of the anolyte solutions were taken. In long duration experiments to assess the efficacy of nitrogen reduction, eHB reactors were used. In certain experiments (Supplementary Fig. 12), the Daramic was replaced with a thinner Celgard separator to promote diffusion between the electrolyte compartments, or the separator was removed completely. 20 mA of current were applied to the reactor, while 5 sccm of N₂ and H₂ flowed past the cathode and anode GDEs, respectively.

To couple the eHB to water splitting, a commercially available water-splitting cell (Fuel Cell Technologies, 5SCH) was assembled. The electrodes were part of a membrane electrode assembly (MEA, 1141002) purchased from FuelCellStore with an electrode area of 5 cm². The cathode side was platinum black with a loading of 3 mg cm⁻²; the anode side was iridium ruthenium oxide with a loading of 3 mg cm⁻²; both electrodes were on a Nafion 115 membrane. The bolts on the electrolyzer were tightened with a torque wrench with a torque of 40 lb-in.

Milli-Q water was fed continuously to the anode of the water splitting cell at ~70 mL/min with a peristaltic pump. A constant current of 200 mA was applied across the electrolyzer; the voltage required was 1.59 V. This corresponds to an output H₂ flowrate of 1.5 sccm. The cell was slightly angled to help oxygen bubbles to leave the anode compartment. The cathode compartment was sealed off at one end to force hydrogen to flow in a single direction. The hydrogen was first fed to a vial containing magnesium sulfate (MgSO₄) to capture some of the moisture in the gas stream, after which it was fed to a vial with THF and molecular sieves to saturate the gas with THF. The cell was then operated analogously to an eHB cell, with the difference that the feed rate of H₂ was 1.5 sccm, as defined by the water splitting current.

Supplementary Discussion

Computing the diffusion-limited current density for H₂ oxidation

We can estimate the diffusion-limited current density for H₂ oxidation and find that it is fairly close to the value we obtain via direct measurement (Fig. 1b). The diffusion-limited current density can be computed via Supplementary Equation 6.⁸

$$J_{lim} = \frac{2D_{H_2}C_{H_2}F}{\delta} \quad (6)$$

The solubility of hydrogen in pure THF is 3.3-3.4 mM.^{9,10} However, the properties of the solvent change with addition of large amounts of electrolyte, leading to a “salting-out” effect, decreasing the solubility of the gas.¹¹ We estimate that the solubility of hydrogen in our electrolyte is close to half of its pure solvent solubility, approximately 1.7±0.8 mM, following a previous analysis.¹ The diffusivity of hydrogen in the electrolyte is also an estimate, computed by using an approximate value of the viscosity of solution,¹ and assumed to be 3.8±0.8·10⁻⁹ m² s⁻¹. The diffusion boundary layer thickness was previously measured and found to be 50±15 μm;¹ corrections to the diffusion boundary layer thickness due to differences in diffusion coefficients of various species are not used due to the already large uncertainties in estimates of other parameters. Combining these assumptions, the estimated diffusion-limited current density for H₂ oxidation is 2.5±1.5 mA cm⁻², which is fairly close to the experimentally measured value (~2.75 mA cm⁻², Fig. 1b).

Development of the gas-liquid interface across the SSC

Supplementary Fig. 2 depicts the development of the gas-liquid interface across the vertical standing SSC and carbon-cloth (CC) GDEs. As the figures may not tell the complete picture, we are describing the process in words below.

Initially, the gas compartment and electrolyte compartments contain no electrolyte and are separated by a vertically standing SSC or CC GDE. When gas is fed to the gas compartment, it predominantly leaves through the GDE if any resistance to flow (by means of water column or otherwise) is applied to the outlet of the gas compartment. When a small volume of electrolyte (880 μL) is added, the SSC and CC GDEs behave differently.

In the case of the CC GDE, the electrolyte completely stays within the electrolyte compartment and wets the GDE, and gas begins to flow out through the gas compartment outlet if there is not sufficient pressure to force the gas through the GDE. Adding additional electrolyte (for a total of 1.75 mL) does not qualitatively change the picture.

In the case of an SSC GDE, the electrolyte actually goes through the vertically standing GDE into the gas compartment (Supplementary Fig. 2). The gas usually escapes through the top of the SSC that has not been wet by electrolyte if any resistance to flow is applied to the outlet of the gas compartment. When additional electrolyte is added (1.75 mL total), there is sufficient electrolyte between the two compartments to fully wet the SSC and prevent gas flow through the GDE until a pressure gradient with a magnitude greater than or equal to the magnitude of the Laplace pressure of the GDE is reached. The gas therefore temporarily accumulates in the gas compartment, and increases the absolute pressure in the gas compartment, evidenced by motion of the gas-liquid boundary in the pressure controlling burette (Supplementary Fig. 17). This elevated pressure actually pushes the electrolyte in the gas compartment through the SSC back into the electrolyte compartment. If the pressure gradient across the SSC reaches the Laplace pressure of the SSC, gas begins to flow through the SSC (Supplementary Figs. 2 and 17). If it is lower, gas flows past the SSC out of the gas compartment (Supplementary Figs. 2 and 17).

Computing the diffusion-limited current density of N₂ reduction

The diffusion-limited current density for nitrogen reduction in a 1 M LiBF₄ in THF electrolyte has been estimated in prior work.¹ By following a procedure similar to the one outlined above and in the aforementioned work, we can estimate the diffusion-limited current density in an aqueous electrolyte at a flooded electrode by using Supplementary Equation 7.

$$J_{lim} = \frac{6D_{N_2}C_{N_2}F}{\delta} \quad (7)$$

The diffusion coefficient and solubility of nitrogen in pure water are well known. At 25°C and 1 bar of N₂ partial pressure, the diffusivity of N₂ in water is $2.01 \pm 0.1 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$,¹² while the solubility is 0.66 mM.¹³ The diffusion boundary layer thickness depends heavily on the hydrodynamics of the electrolyte; typical values for CO₂ reduction in an aqueous electrolyte are 60-160 μm ;¹⁴ the boundary layer thickness may be smaller with well-defined and vigorous hydrodynamics, such as in systems utilizing rotating disk electrodes (RDEs). From these values, we find that the diffusion limited current density for nitrogen reduction in water is a mere 0.48-1.27 mA cm⁻².

Source of ammonia in two phases

We found that produced NH₃ can be found in both the solution and the gas phases (Fig. 3c, d). The rate at which NH₃ is produced in the gas phase is almost independent of the applied current density, which implies that the FE for NH₃ in the gas phase decreases with applied current density. It is unlikely that the NH₃ is formed directly in the gas phase, as both the lithium and proton source required for NH₃ formation are in solution. The source of NH₃ in the gas phase may be stripping of the solution of NH₃ by the gas flowing past the SSC. This would imply that NH₃ is much more concentrated at the electrode than in the bulk. The general lack of forced mixing in the electrolyte supports this hypothesis. No ammonia is found in the gas phase when gas flows through the electrode (Fig. 3d). Any gas phase ammonia would be diluted in the bulk solution and thoroughly mixed, minimizing the amount of stripping.

The lack of stripping of ammonia from the bulk solution is likely due to strong interactions between Li⁺ and NH₃, stronger than between Li⁺ and THF.¹⁵ The formation Li-NH₃ complexes in solution increases the solubility of ammonia in the electrolyte (Supplementary Fig. 24), reducing the ammonia partial pressure at a given NH₃ concentration.

Estimating energy efficiency and consumption

A detailed description for estimating the energy efficiency of the process and sources of energy losses has been described in prior work.¹ Briefly, the energy efficiency is computed as follows by the formula given in Supplementary Equation 8.

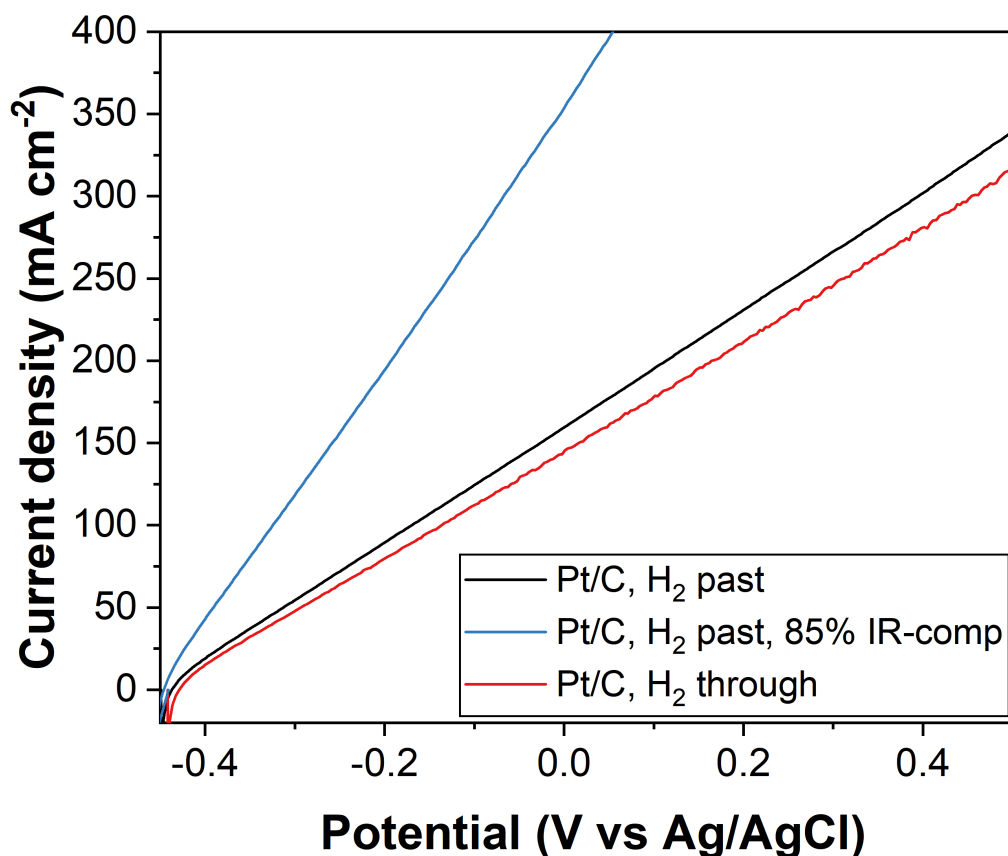
$$\eta = \frac{U_{NH_3} \cdot FE}{V_{total}} \quad (8)$$

In Supplementary Equation 8, U_{NH_3} is the standard potential for the reaction of ammonia oxidation, i.e. the one likely to be used to extract useful work ($4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$), V_{total} is the total applied potential across the cell, and FE is the Faradaic efficiency. In order to compute the energy consumption, Supplementary Equation 9 was used.

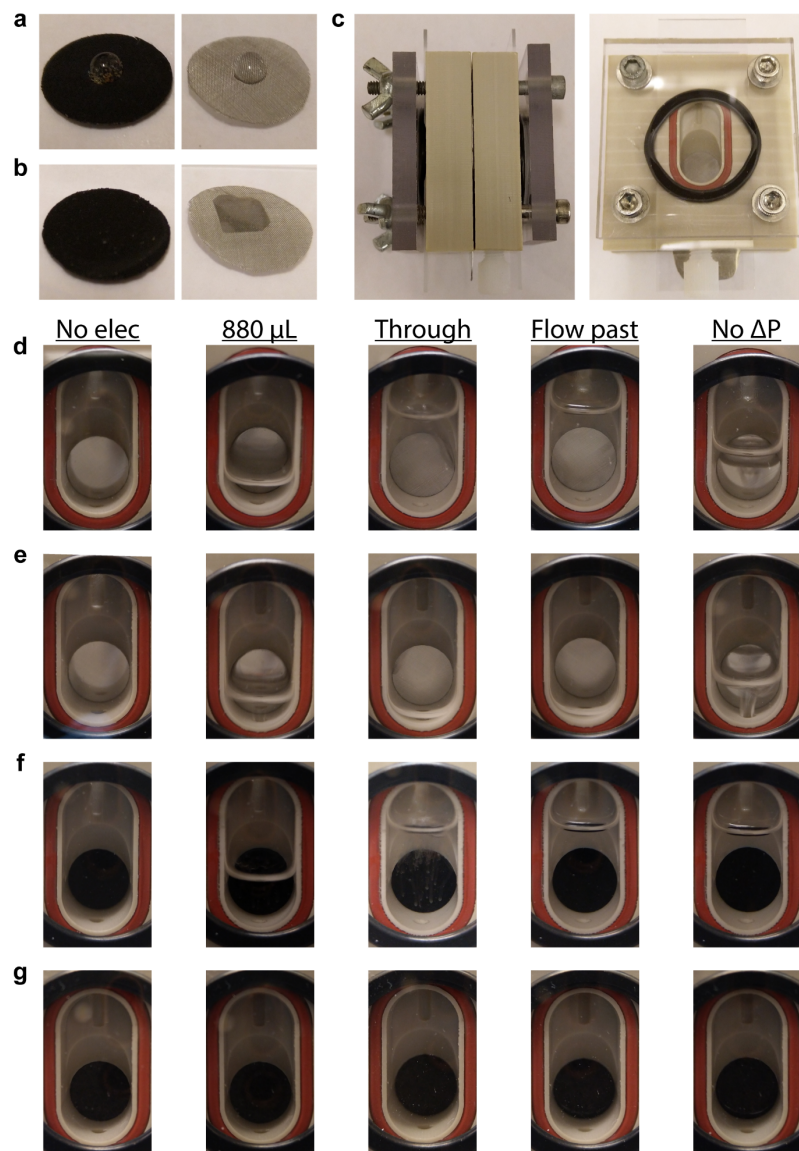
$$P = \frac{3F \cdot V_{total}}{FE \cdot M_{NH_3}} \quad (9)$$

In Supplementary Equation 9, F is Faraday's constant (96485 C/mol), V_{total} is the total applied cell voltage, FE is the ammonia Faradaic efficiency, and M_{NH_3} is the molar mass of ammonia.

Supplementary Figures

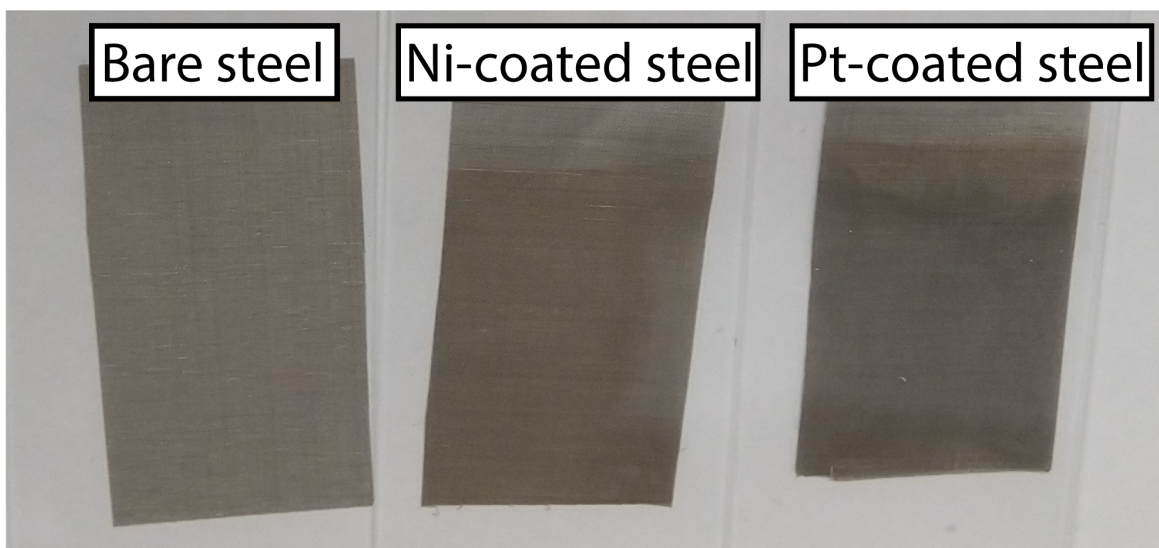


Supplementary Fig. 1. Linear sweep voltammograms of hydrogen oxidation on gas diffusion electrodes in 0.5 M H₂SO₄ in water. The sweep rate used is 5 mV s⁻¹. Hydrogen oxidation occurs at high rates on hydrophobic platinum-loaded carbon paper (Pt/C) both when gas flows past the GDE (no pressure gradient applied) and when it flows through the GDE in an aqueous solution. Resistive losses account for most of the potential applied. When using software resistance compensation (compensated 85% of 1.7 Ohm resistance that was determined by the software using impedance spectroscopy), the current-potential curve shifts, but does not change shape significantly. The high rates of hydrogen oxidation on GDEs in aqueous solvents demonstrate that it is in fact a change of solvent from aqueous to nonaqueous (Fig. 3a) that leads to poor hydrogen oxidation rates and FEs on carbon fiber GDEs.

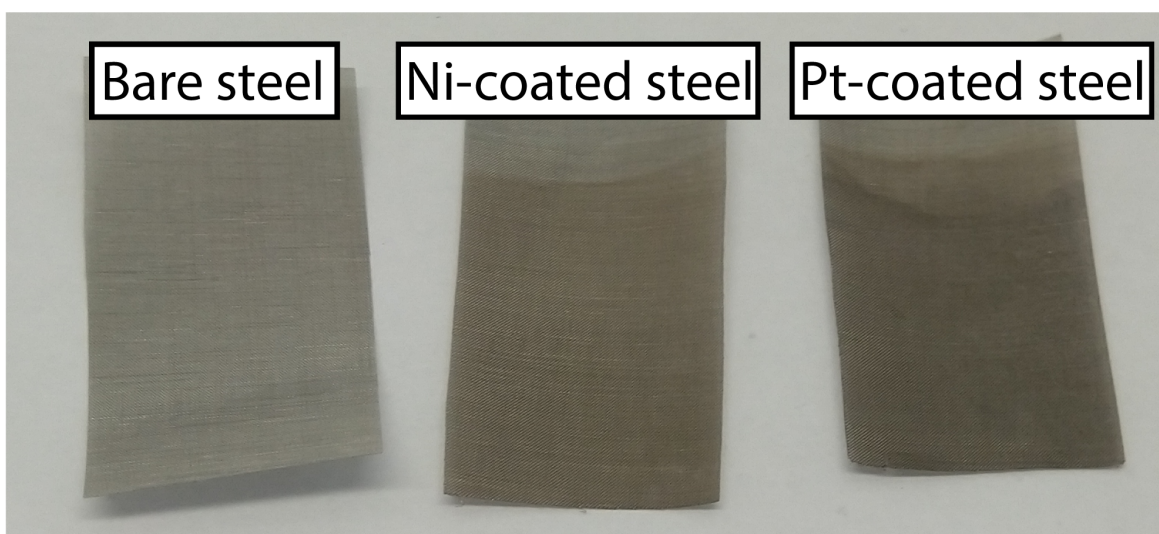


Supplementary Fig. 2. Establishment of a gas-liquid boundary in the cell. (a) 20 μ L of water on platinum-loaded carbon paper (left, Pt/C) and stainless steel cloth (right, SSC). The water droplet beads up on both materials. (b) 20 μ L of 1 M LiBF₄, 0.11 M EtOH, THF (the electrolyte), on Pt/C and SSC. The electrolyte penetrated into the Pt/C and spread through it, while the spreading was finite on steel cloth, demonstrating the lack of capillary action on the SSC. (c) Side and front photos of modified cell used to image the gas and electrolyte compartments. A glass slide is used in place of a PEEK back plate and membrane for the gas and electrolyte compartments, respectively. O-rings are used to evenly distribute pressure on the glass slides, and polycarbonate back plates are used to hold the structure together. The compartments are imaged without electrolyte (“no elec”), with half the usual volume of electrolyte (“880 μ L”), with the usual volume of electrolyte of 1.75 mL and gas flowing through the electrode (“through”), gas flowing past the electrode at 1 kPa (“flow past”), and under lack of pressure gradient (“no Δ P”). (d) The electrolyte compartment when using an SSC. (e) The gas compartment when using an SSC. (f) The electrolyte compartment when using Pt/C. (g) The gas compartment when using Pt/C.

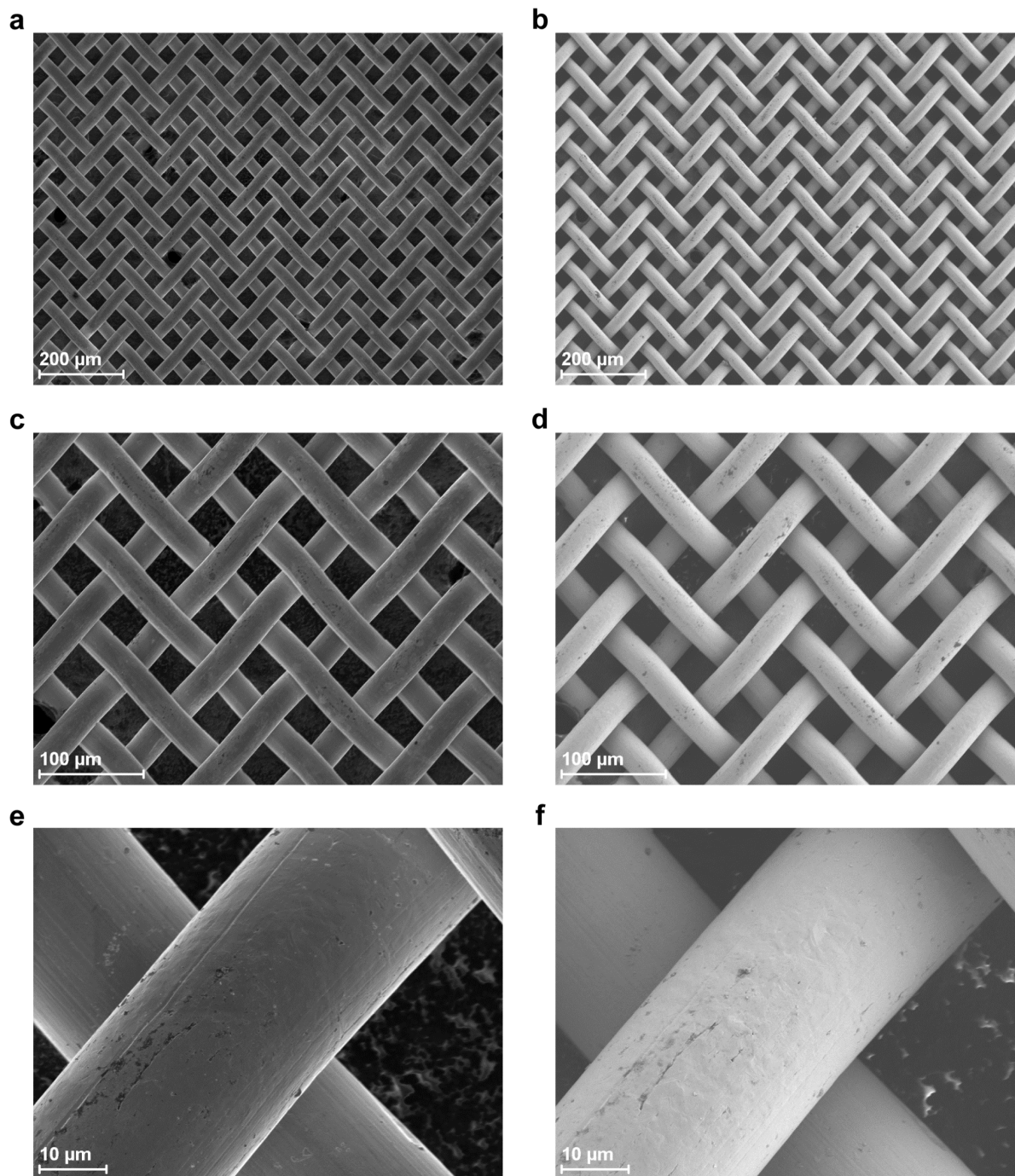
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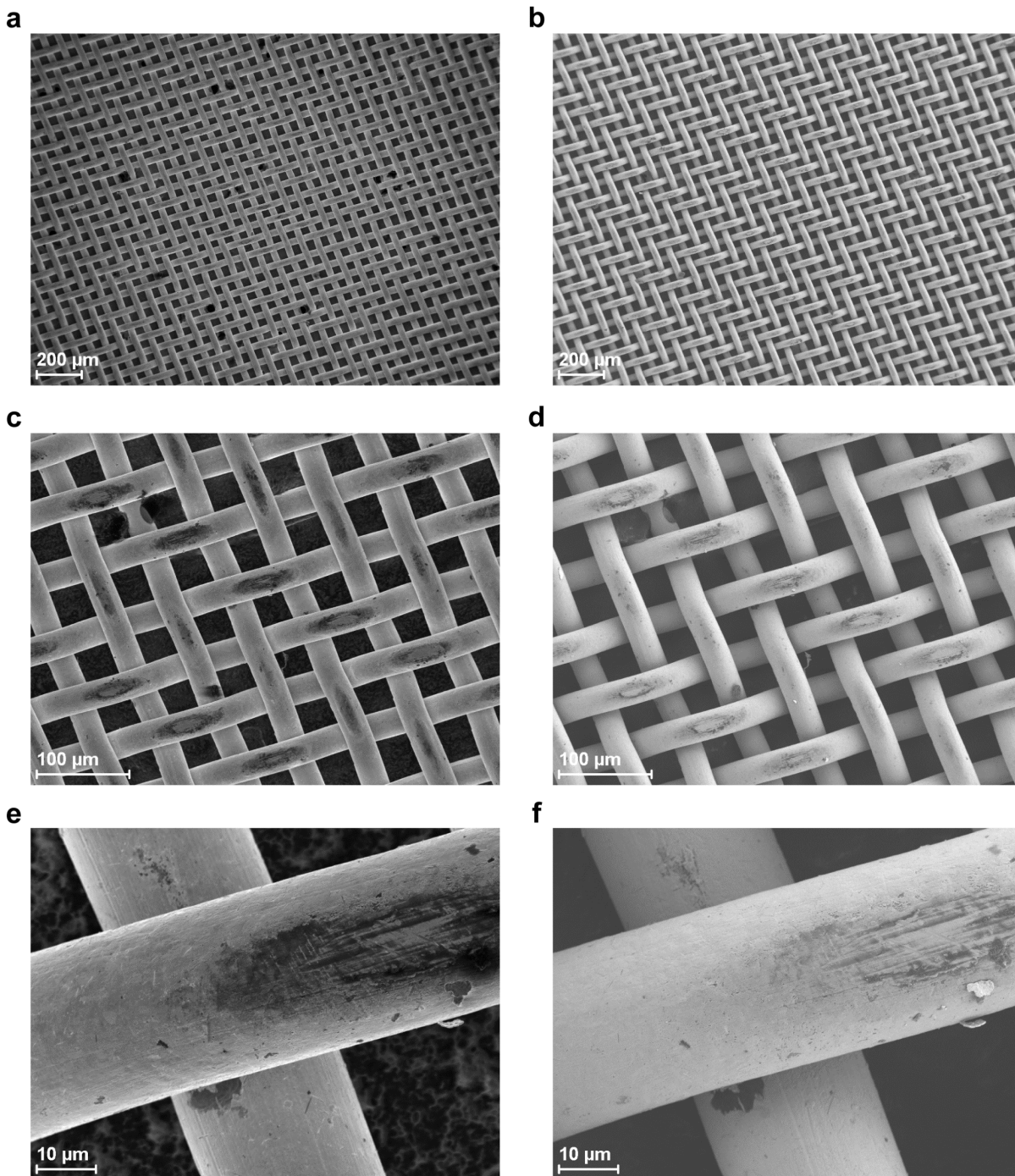
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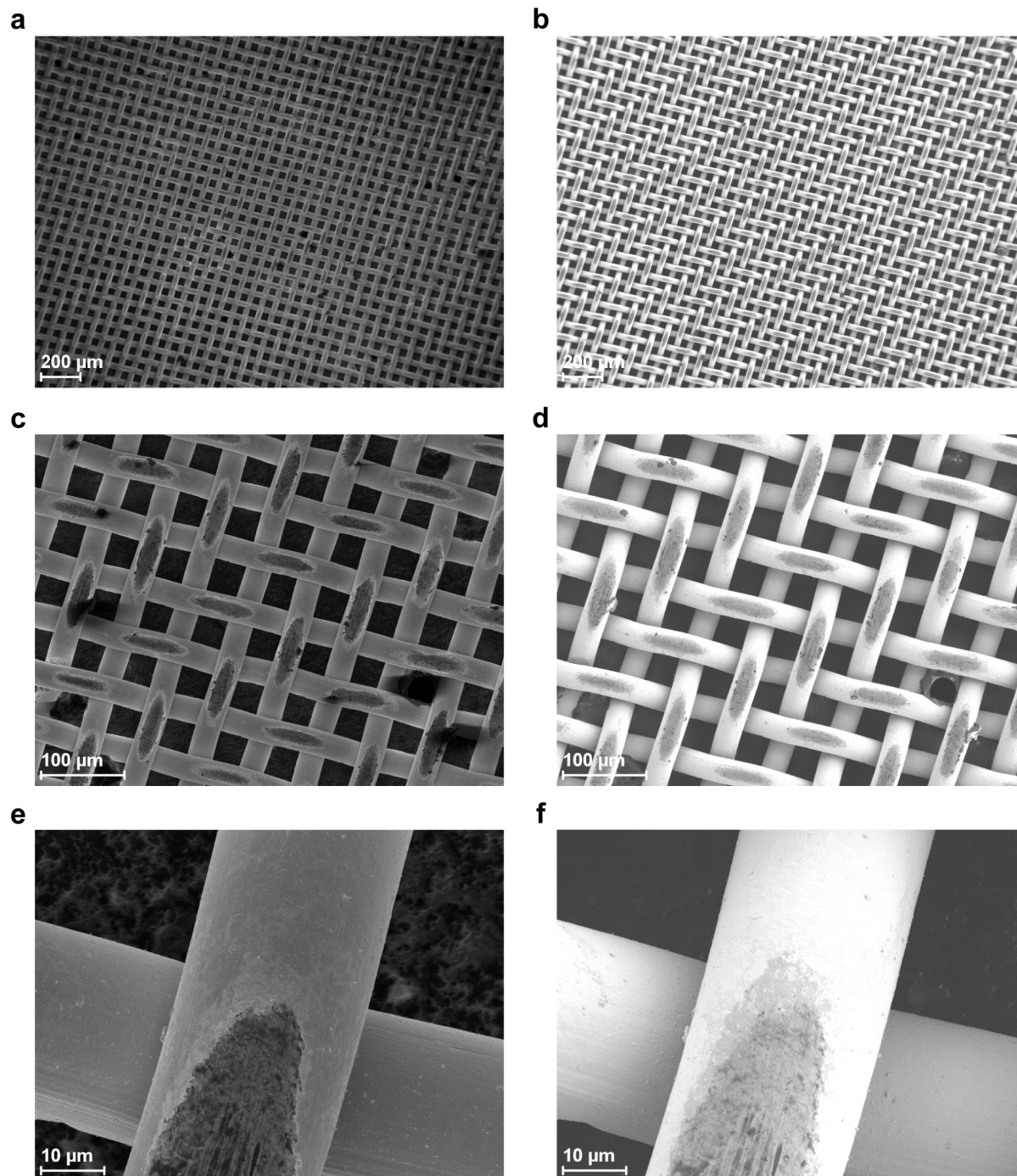
Supplementary Fig. 3. Images of various stages of plating platinum onto steel cloths. Note that the cloths have been cut into smaller pieces after metal plating for ease of presentation. **(a)** Steel cloths under glass slides. **(b)** Freely moving steel cloths. Note the brown tint that appears after striking the cloths with nickel, and the darker, black tint that appears after plating platinum onto the nickel.



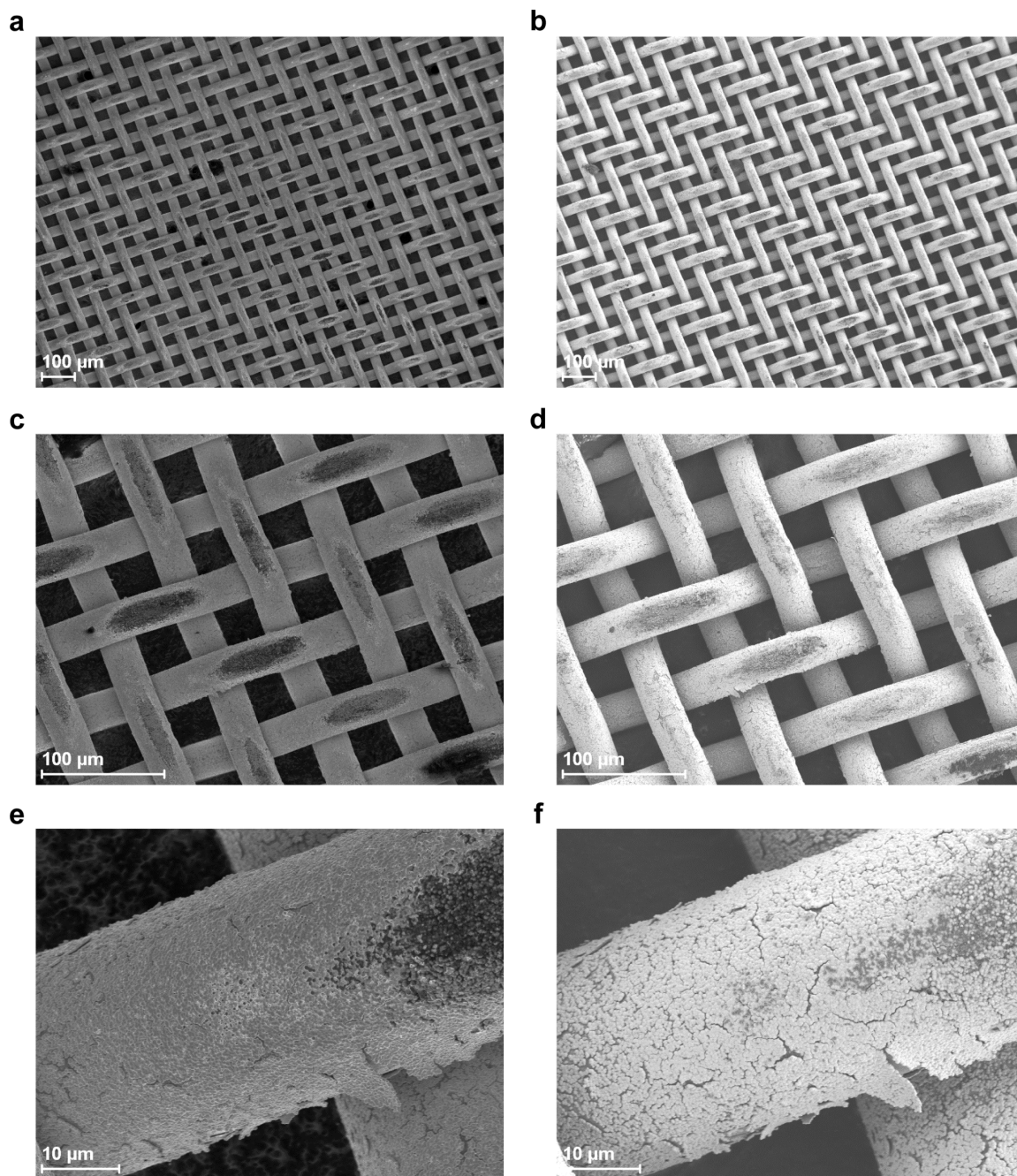
Supplementary Fig. 4. Scanning electron microscopy (SEM) images of bare stainless steel cloths. A Zeiss-Merlin HR-SEM was used to collect images. (a, b) Low magnification. (c, d) Medium magnification. (e, f) High magnification. Panels (a, c, e) used an Inlens detector, while (b, d, f) used an HE-SE2 detector.



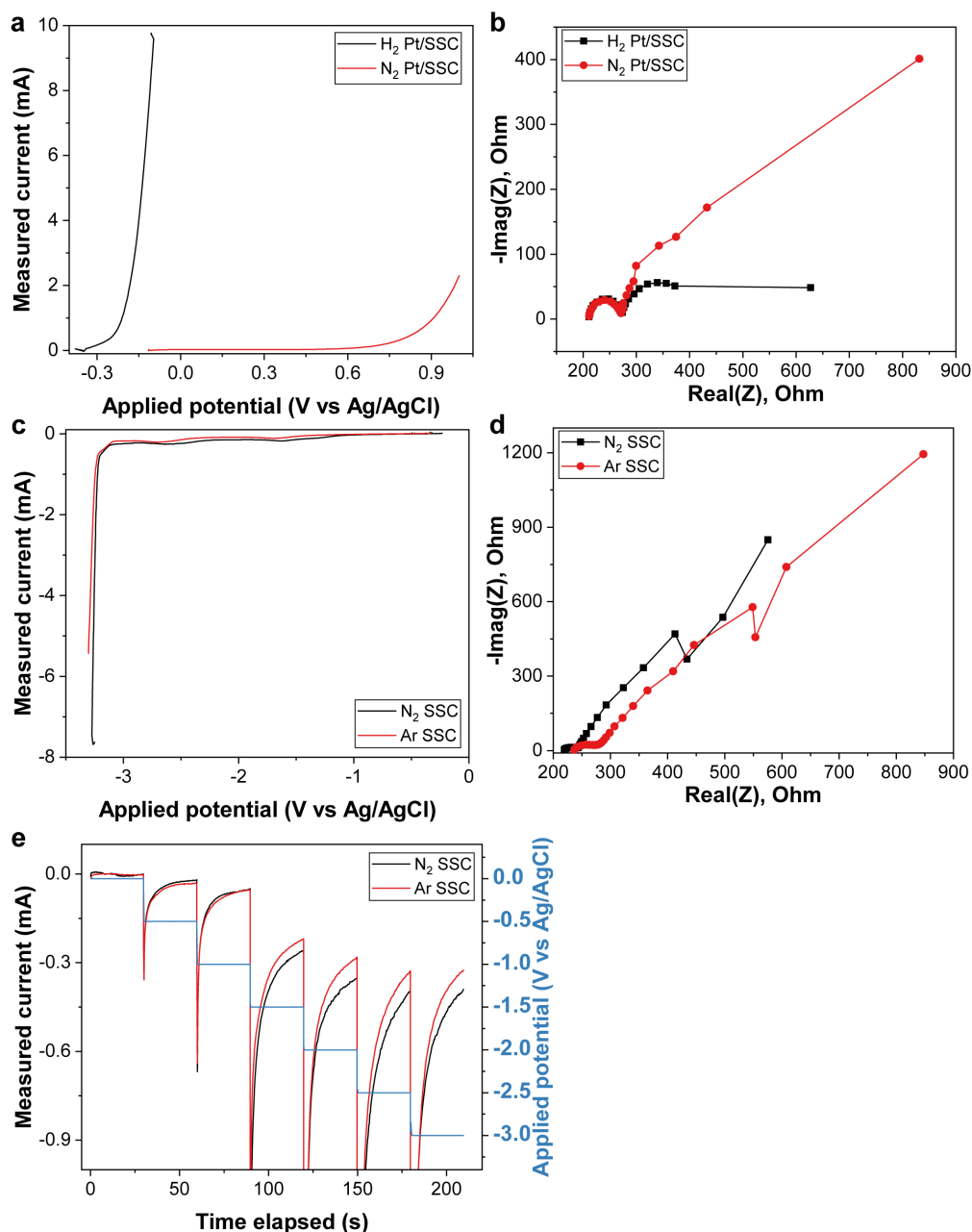
Supplementary Fig. 5. Scanning electron microscopy (SEM) images of nickel-coated stainless steel cloths. A Zeiss-Merlin HR-SEM was used to collect images. (a, b) Low magnification. (c, d) Medium magnification. (e, f) High magnification. Panels (a, c, e) used an Inlens detector, while (b, d, f) used an HE-SE2 detector. Note the uncoated sections at the top of the threads. They are likely formed when one side of the cloth contacts the glass wall in the beaker cell used for nickel striking (i.e. from poor transport of Ni^{2+} to the surface).



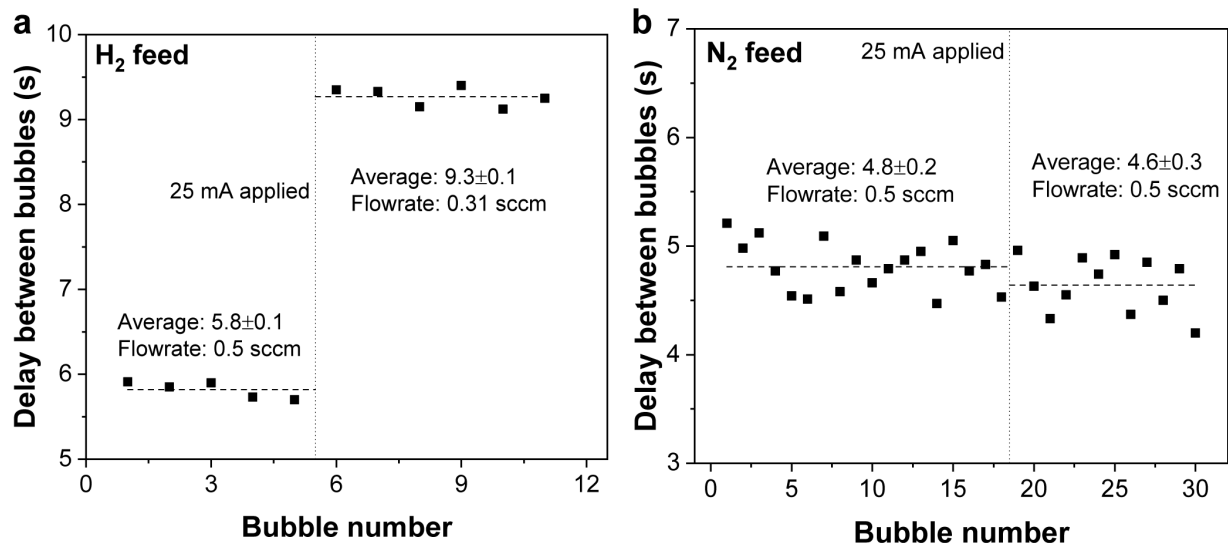
Supplementary Fig. 6. Scanning electron microscopy (SEM) images of smoothly Pt-coated stainless steel cloths. A Zeiss-Merlin HR-SEM was used to collect images. (a, b) Low magnification. (c, d) Medium magnification. (e, f) High magnification. Panels (a, c, e) used an Inlens detector, while (b, d, f) used an HE-SE2 detector. Note the poorly coated regions at the top of the threads. As platinum poorly adheres to stainless steel, they are likely caused by the Ni-less regions observed in Ni plated cloths (Supplementary Fig. 5).



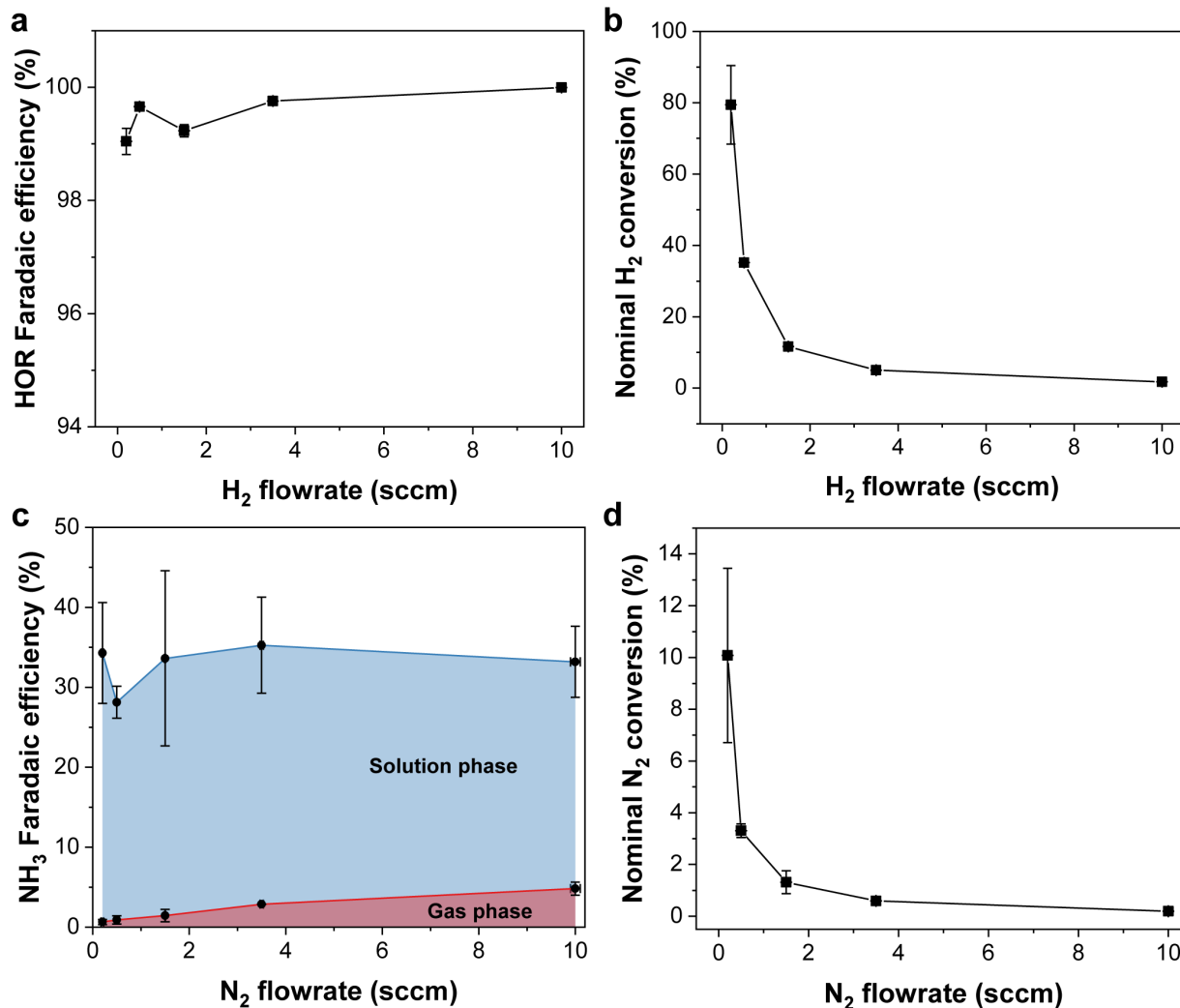
Supplementary Fig. 7. Scanning electron microscopy (SEM) images of roughly Pt-coated stainless steel cloths. A Zeiss-Merlin HR-SEM was used to collect images. (a, b) Low magnification. (c, d) Medium magnification. (e, f) High magnification. Panels (a, c, e) use an Inlens detector, while (b, d, f) used an HE-SE2 detector. Regions of poor platinum coating are visible as in Supplementary Fig. 6. The platinum coating here does not adhere to the threads as well, leading to rougher surfaces. The measured HOR FE is unaffected up to at least 25 mA cm^{-2} of applied current density, with similar performance as the smoothly coated Pt from Supplementary Fig. 6. From the same plating protocol, both smooth and rough platinum are observed, but their performance is not distinguishable during hydrogen oxidation.



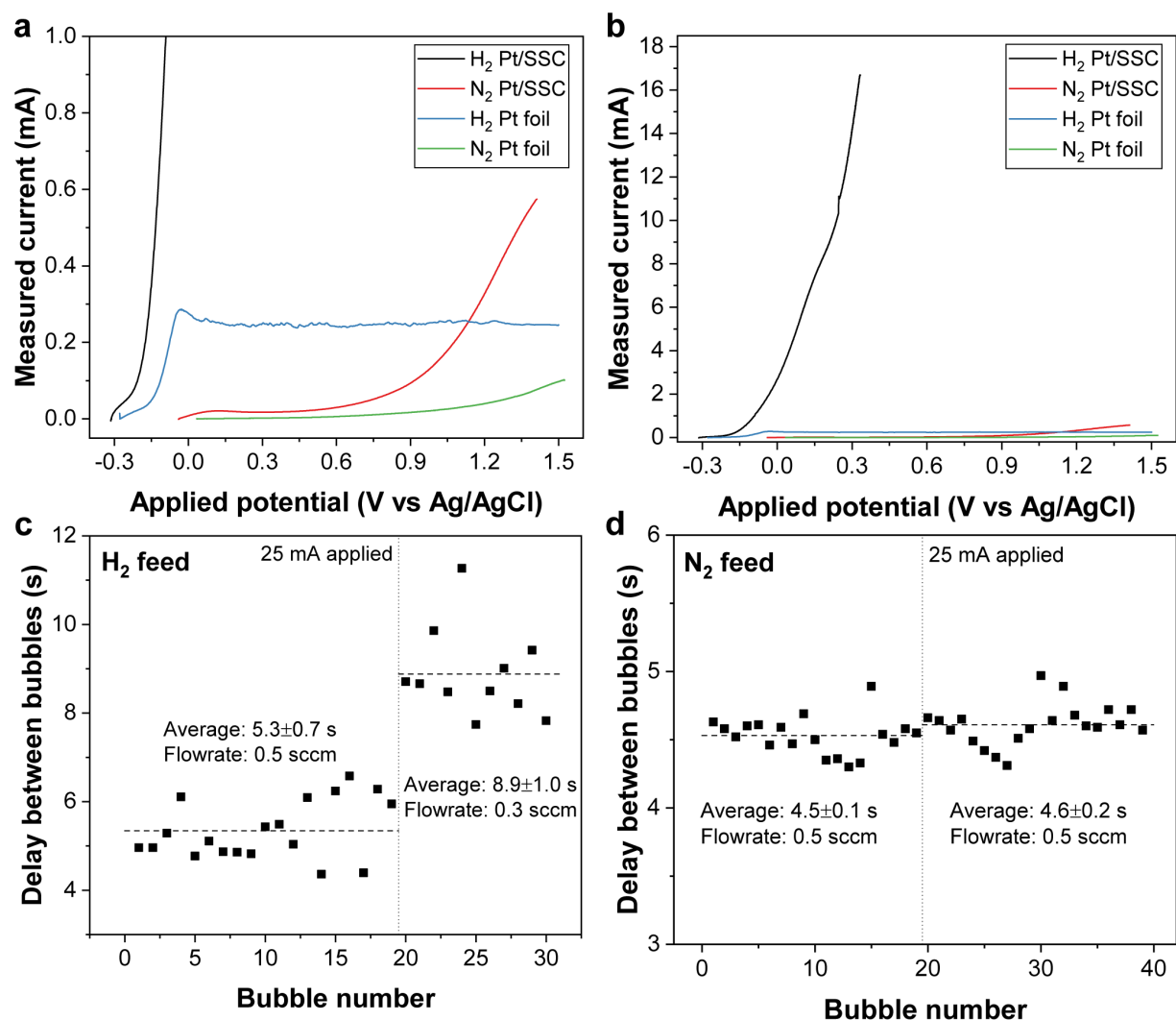
Supplementary Fig. 8. Electrochemical characterization of SSC and Pt/SSC electrodes. A 1 M LiBF₄/0.11 M EtOH/THF electrolyte was used in a 3-compartment cell with an Ag/AgCl pseudoreference for all experiments with 100% software resistance compensation. The resistance was measured by PEIS. **(a)** Linear sweep voltammograms of Pt/SSC when H₂ or N₂ are flowed past the electrode at 10 sccm and a 1 kPa gradient across the electrode. The high oxidation currents visible when H₂ is fed to the electrode support the notion that HOR is occurring. **(b)** Impedance spectra of the system in **(a)**. **(c)** Linear sweep voltammograms of SSC when N₂ or Ar are flowed past the electrode at 10 sccm and a 1 kPa gradient across the electrode. **(d)** Impedance spectra of the system in **(c)**. **(e)** Constant potential holds of the system in **(c)**. Note that potential overloads in PEIS prevented measurement of additional points at lower frequencies. Linear sweep voltammograms were collected at a sweep rate of 5 mV s⁻¹.



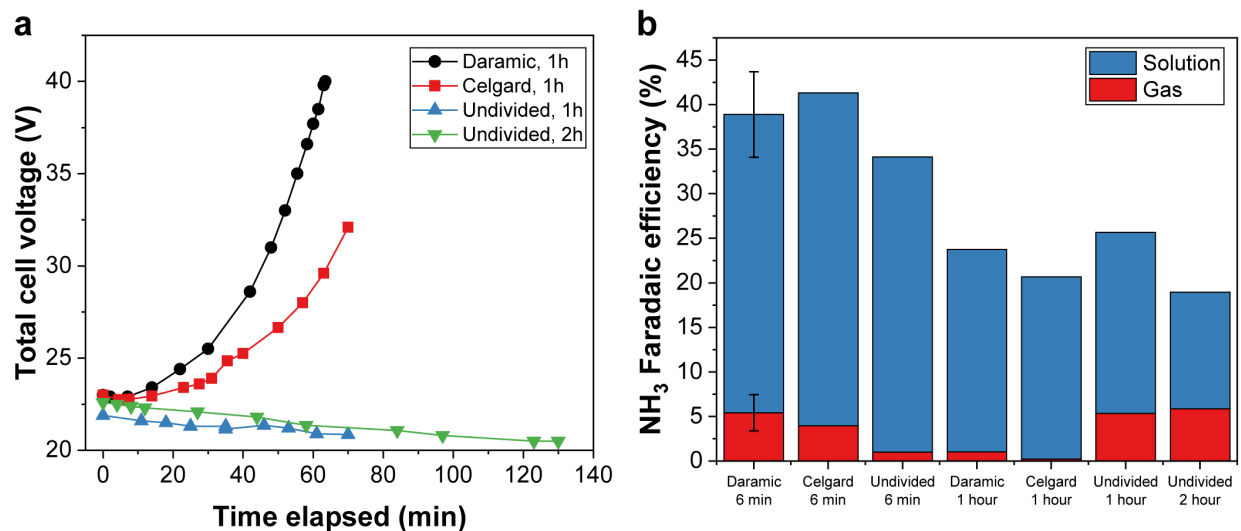
Supplementary Fig. 9. Hydrogen mass balance-based quantification of HOR FE. A 1 M LiBF₄/0.11 M EtOH/THF electrolyte was used in a 3-compartment cell with a Pt/SSC anode for hydrogen oxidation quantification. The time required for successive bubbles of gas to leave the gas compartment (see Supplementary Fig. 17) was recorded for **(a)** H₂ and **(b)** N₂ feed gases before and after application of 25 mA of current. When H₂ was used as the feed, the time required for bubbles to evolve decreased when current was applied because H₂ was being consumed at the electrode, while no change was observed when N₂ was used as the feed. The FE towards HOR was found to be $105 \pm 2\%$, i.e. close to unity.



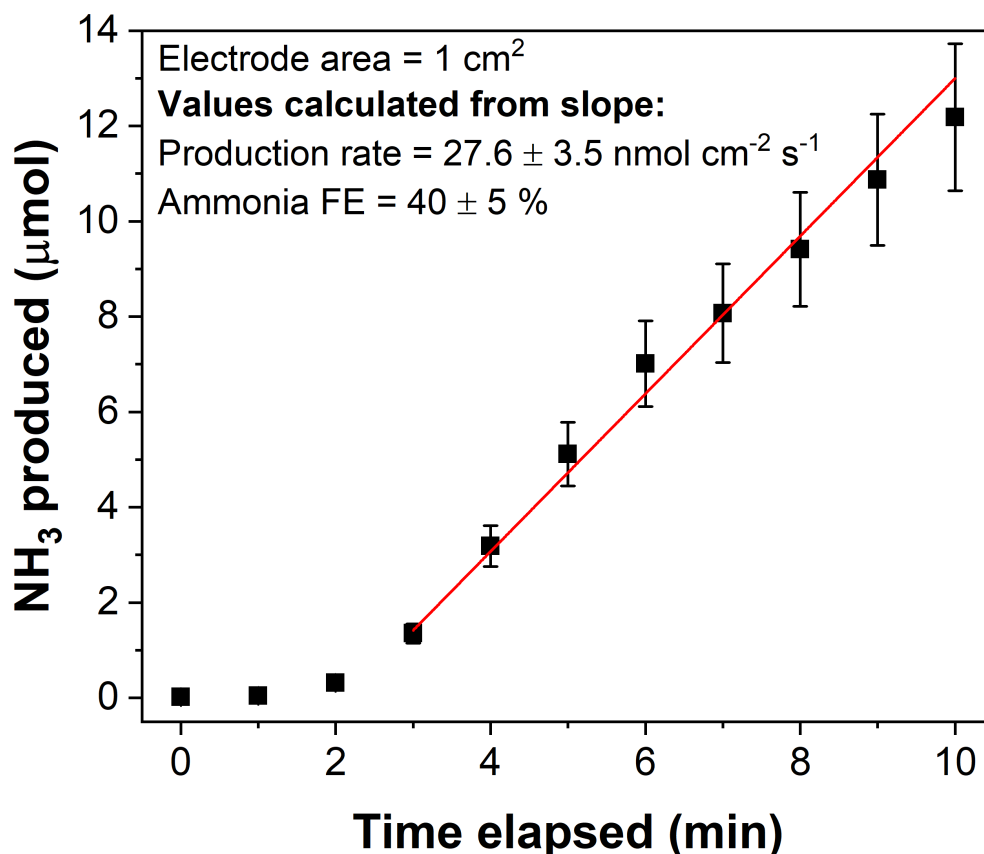
Supplementary Fig. 10. The effect of flowrate of feed gas past SSC-based GDEs in electrochemical experiments at an applied current density of 25 mA cm^{-2} . (a) The effect of H₂ flowrate on HOR FE. Note that no significant trend in HOR FE is observed when changing the flowrate; the FE is >99% in all cases. (b) The nominal single-pass conversion of H₂ as a function of flowrate. At low flowrates (~ 0.2 sccm), the conversion of H₂ is high; when hydrogen is fed at a rate corresponding to 100% conversion (0.176 sccm), depletion of hydrogen and a lowering of the pressure gradient across the Pt/SSC is observed, so a higher flowrate is required to maintain stable operation. (c) The effect of flowrate on NH₃ FE. Note that at lower flowrates, less ammonia is found in the gas phase, while the total amount of ammonia is unchanged with flowrate. (d) The nominal single-pass conversion of N₂ as a function of flowrate. The residence time for the gases in the gas compartment ranges from 8.2 minutes at 0.2 sccm to 10 seconds at 10 sccm. Vertical error bars in (a) represent the uncertainty in the FE measurement for a single run. Vertical error bars in (b, d) represent the error in conversion, computed from the uncertainties in flowrate and FE. Vertical error bars in (c) represent the standard deviation of multiple replicates of the same experiment ($n \geq 2$). Horizontal error bars represent the uncertainty in gas flowrate.



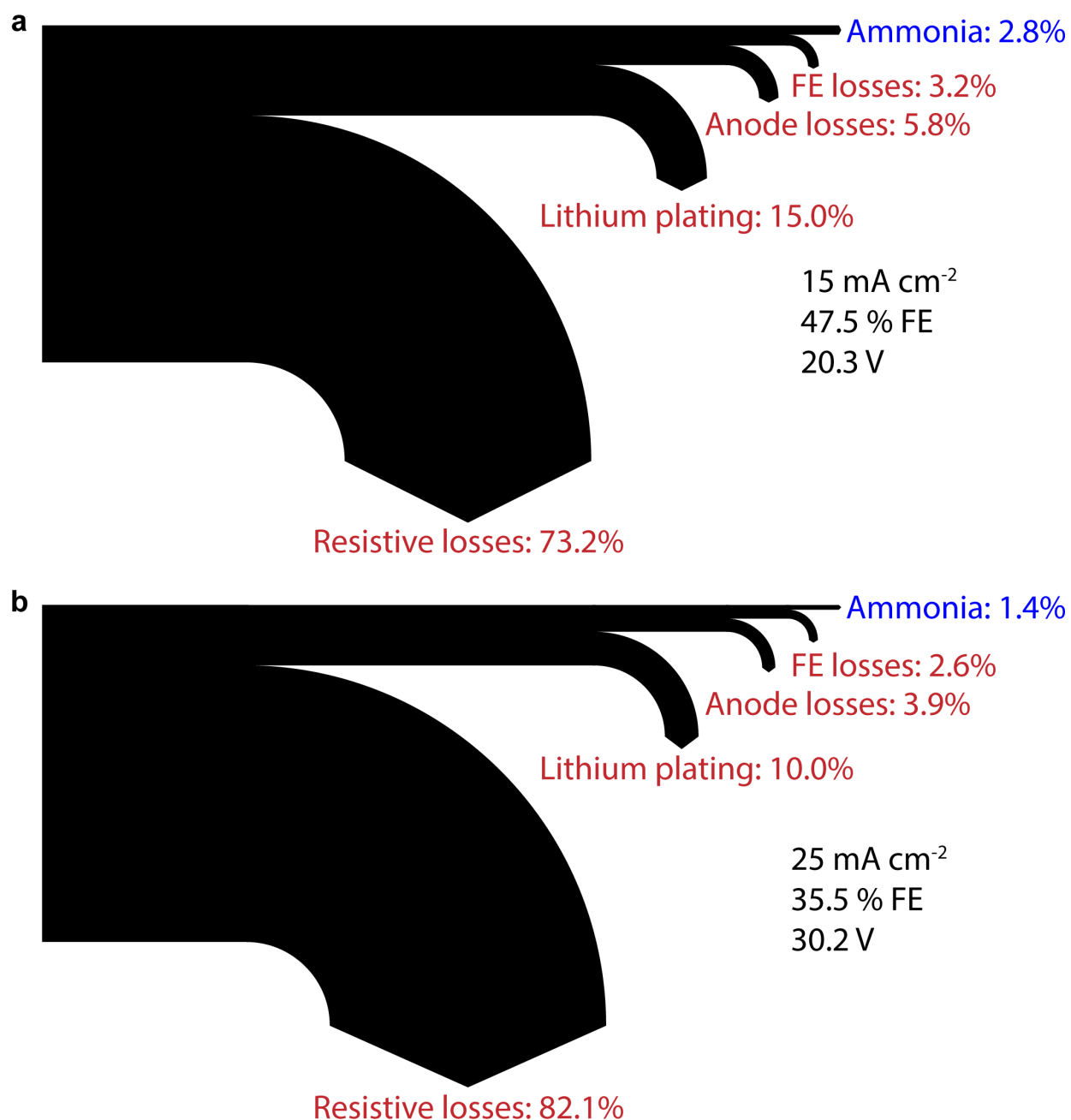
Supplementary Fig. 11. Use of Pt/SSC for hydrogen oxidation in propylene carbonate-based electrolyte. A 1 M LiBF₄ in 9:1 propylene carbonate/dimethyl carbonate was used to demonstrate the efficacy of Pt/SSC for hydrogen oxidation. **(a)** Linear sweep voltammograms (LSVs) collected at a sweep rate of 5 mV s⁻¹ for flooded and GDE configurations. The respective gases (N₂ and H₂) were fed through the electrolyte at 10 sccm for the flooded (Pt foil) case, or past the Pt/SSC at 10 sccm for the GDE (Pt/SSC) case. **(b)** The same data as depicted in **(a)**, but with a larger range of current values shown to demonstrate the high H₂ oxidation current obtained when using a Pt/SSC. Higher potentials (and currents) were not possible to apply using the VMP3 potentiostat, which is necessary for three-electrode electrochemical measurements, as the total cell voltage exceeded its operating range (~10 V). **(c, d)** Time intervals between gas bubbles leaving the gas compartment of the 3-compartment cell used in Pt/SSC experiments with a propylene carbonate based-electrolyte when **(c)** H₂ or **(d)** N₂ was used as the feed gas. The computed Faradaic efficiency towards H₂ oxidation is 112±19%, while it is 5±5% when N₂ is fed to the anode.



Supplementary Fig. 12. Potentials and Faradaic efficiencies toward NH₃ in long duration experiments when using an eHB reactor. (a) The total cell voltage required for a 20 mA constant current in experiments utilizing a SSC cathode and a Pt/SSC anode with various separators. (b) The Faradaic efficiency toward NH₃ in the aforementioned experiments. Note that in the “undivided 2 hour” experiment, polarization was maintained for 130 minutes. Vertical error bars for the Daramic 6 minute experiment in (b) represent the standard deviation of multiple replicates of the same experiment ($n = 3$). The Faradaic efficiency toward NH₃ decreases from ~38% in short duration experiments to ~20% in longer duration experiments, but is fairly independent of the separator used. When a separator (Celgard or Daramic) between the anode and cathode compartments (Supplementary Fig. 16) is used, the cell voltage increases with time for unknown reasons. We would like to note that separators used here are unoptimized for the chemistry and the reason for the increase in voltage is not clear. Both of these are potential directions for future work. Possible reasons include selective depletion of Li⁺ ions in the catholyte and separator fouling. In an undivided cell, no separator is used, which means that the electrolyte is free to convect between the electrodes.

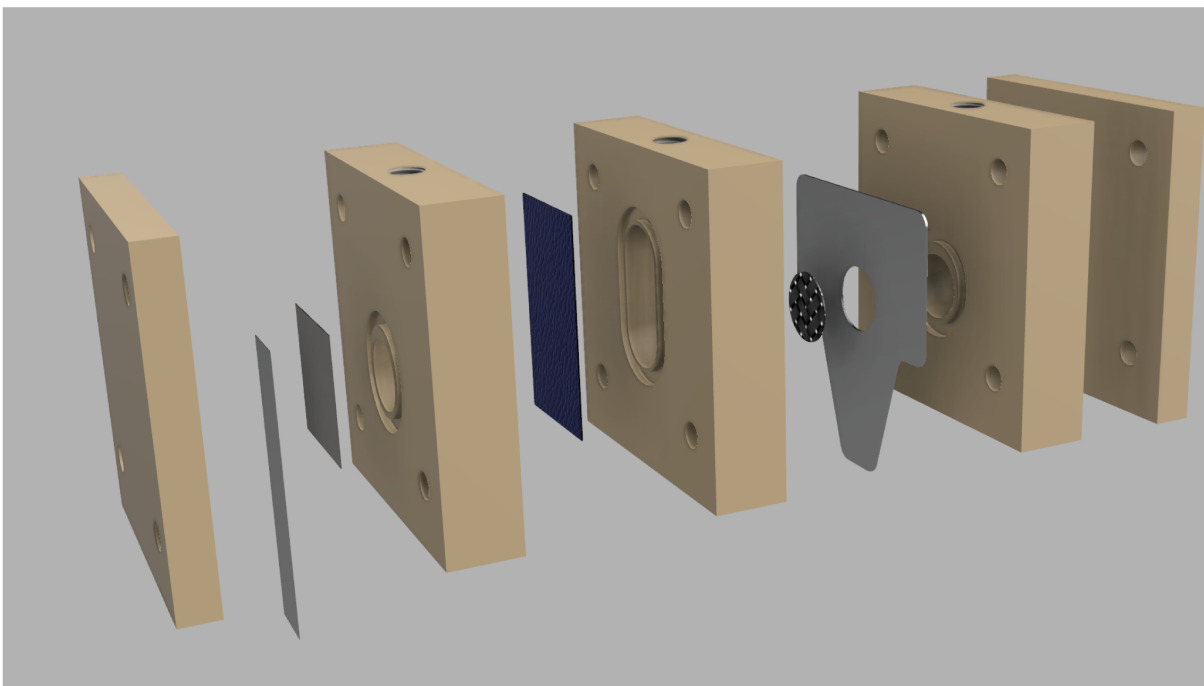


Supplementary Fig. 13. Accumulation of ammonia over time in the electrolyte when using an SSC. The amount of ammonia increases monotonically with time when 20 mA cm⁻² are applied to a cell with an SSC cathode after an induction period of approximately 2 minutes. The short induction period suggests that the lithium-mediated catalytic cycle reaches steady state rapidly. The amount of ammonia produced is estimated by diluting small fractions of the catholyte during operation, as described in *Nitrogen reduction experiments – time evolution of ammonia*. The total amount of ammonia produced in this experiment was measured after the experiment by utilizing the entire catholyte and was found to be 14.5 ± 1 μmol. Vertical error bars represent a combination of estimates of the error associated with ammonia quantification and electrolyte extraction from the cell. In this experiment, the production rate and Faradaic efficiency for ammonia are computed from the slope of the linear fit of data.

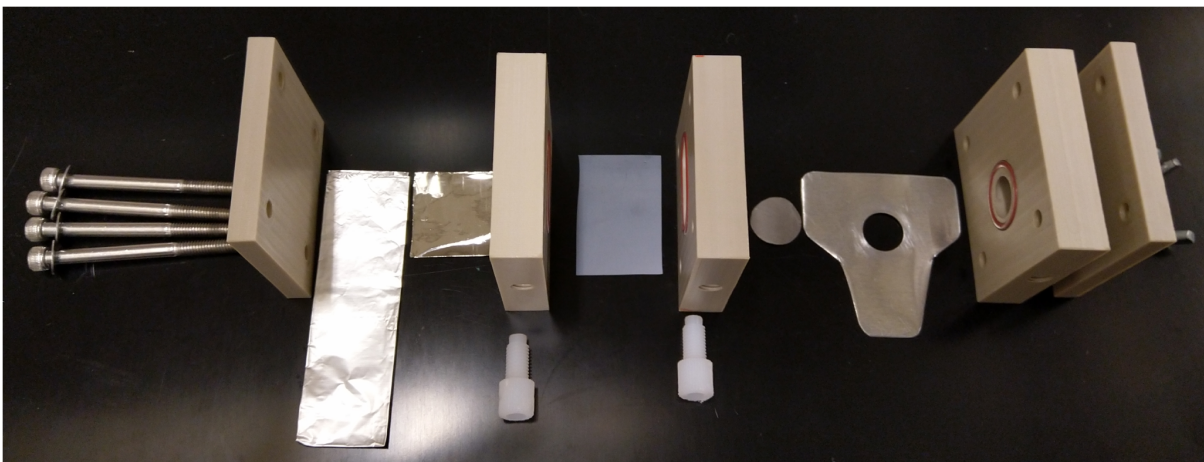


Supplementary Fig. 14. Electrical energy losses in the ammonia production system. (a) Electrical energy losses at high FE conditions (15 mA cm⁻² applied current density, 0.5 kPa pressure gradient across steel cloth). (b) Electrical energy losses at high rate conditions (25 mA cm⁻² applied current density, 1 kPa pressure gradient across steel cloth). Note that the anode reaction is assumed to be THF oxidation, as it was used in the experiments without coupled HOR, hence it is somewhat inefficient. Most of the electrical losses are due to high solution resistance. The procedure to calculate these parameters was described in the Supplementary Discussion and previous work.¹

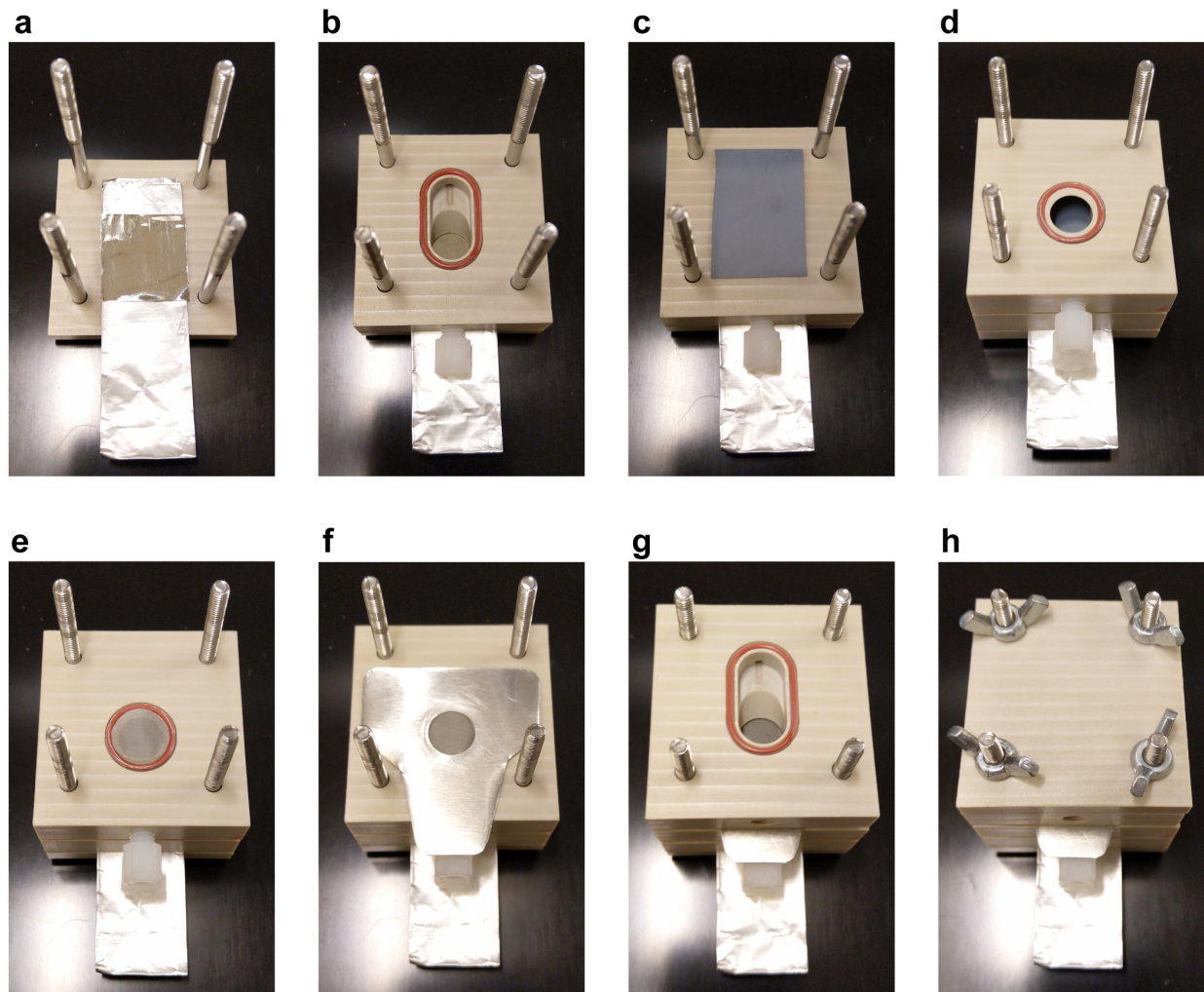
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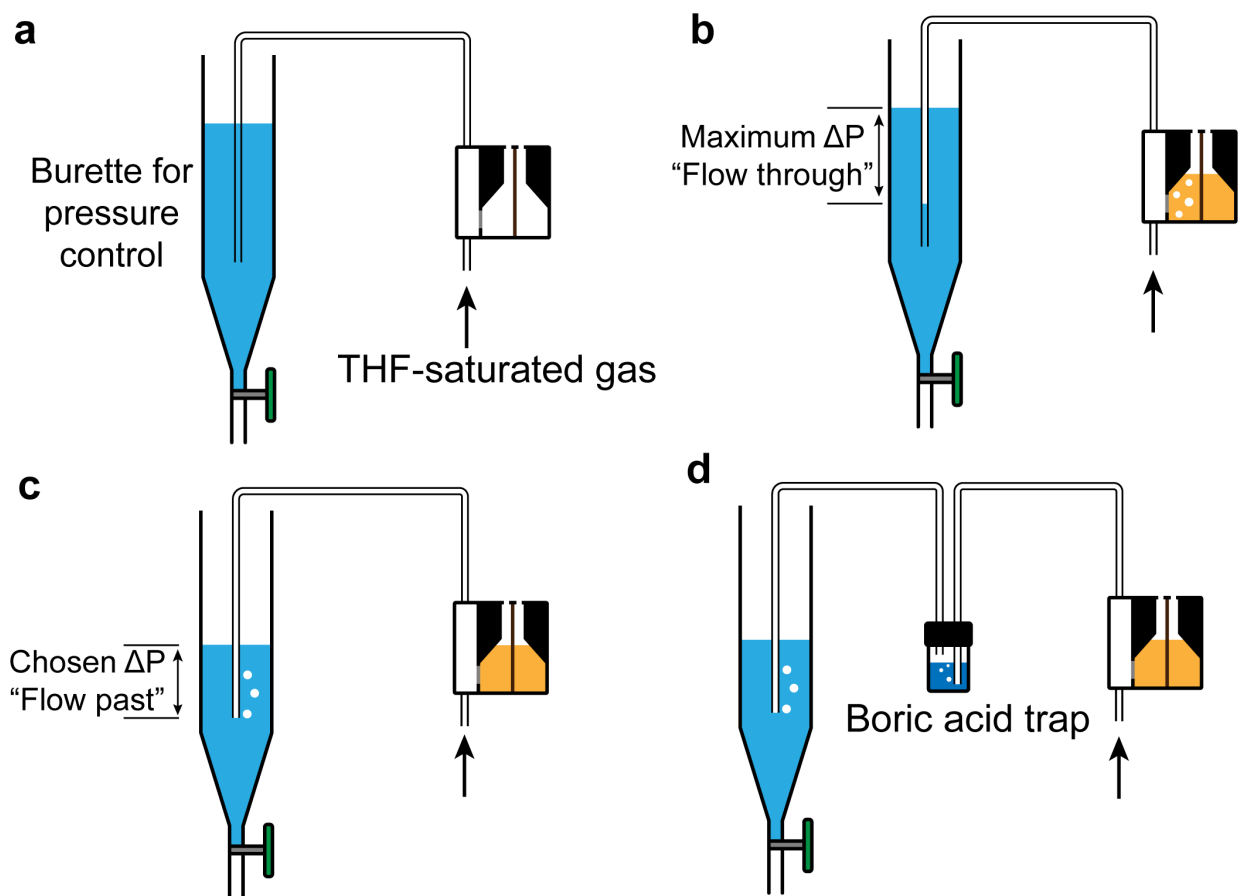
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Supplementary Fig. 15. Depictions of the 3-compartment cell used for GDE experiments. (a) A 3D model of the 3-compartment cell used in GDE experiments. Note: O-rings are not shown. **(b)** A photograph of the parts used to assemble a 3-compartment cell. The cell is made of polyether ether ketone (PEEK) plastic. The cell is inspired by a design used in the CO₂ reduction literature.¹⁶ The cells were machined in-house; CAD and CAM files are available upon request.

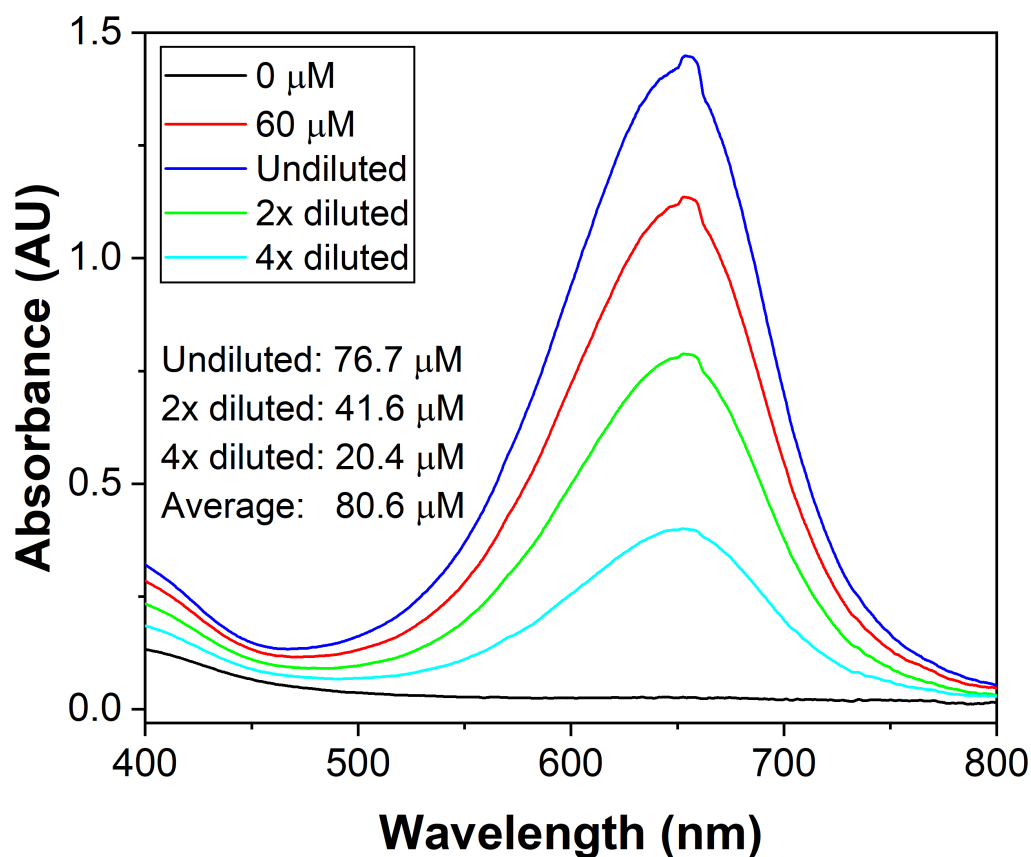


Supplementary Fig. 16. Assembly of a 3-compartment cell in order. The procedure is described in *Assembly of a 3-compartment cell*. (a) The counter electrode and current collector, here a piece of platinum foil and aluminum foil, respectively. (b) The counter electrolyte compartment. (c) The Daramic polyporous separator. (d) The working electrolyte compartment. (e) The gas diffusion electrode, here a stainless steel cloth. (f) The aluminum current collector for gas flow. (g) The gas compartment. (h) The sealed cell.

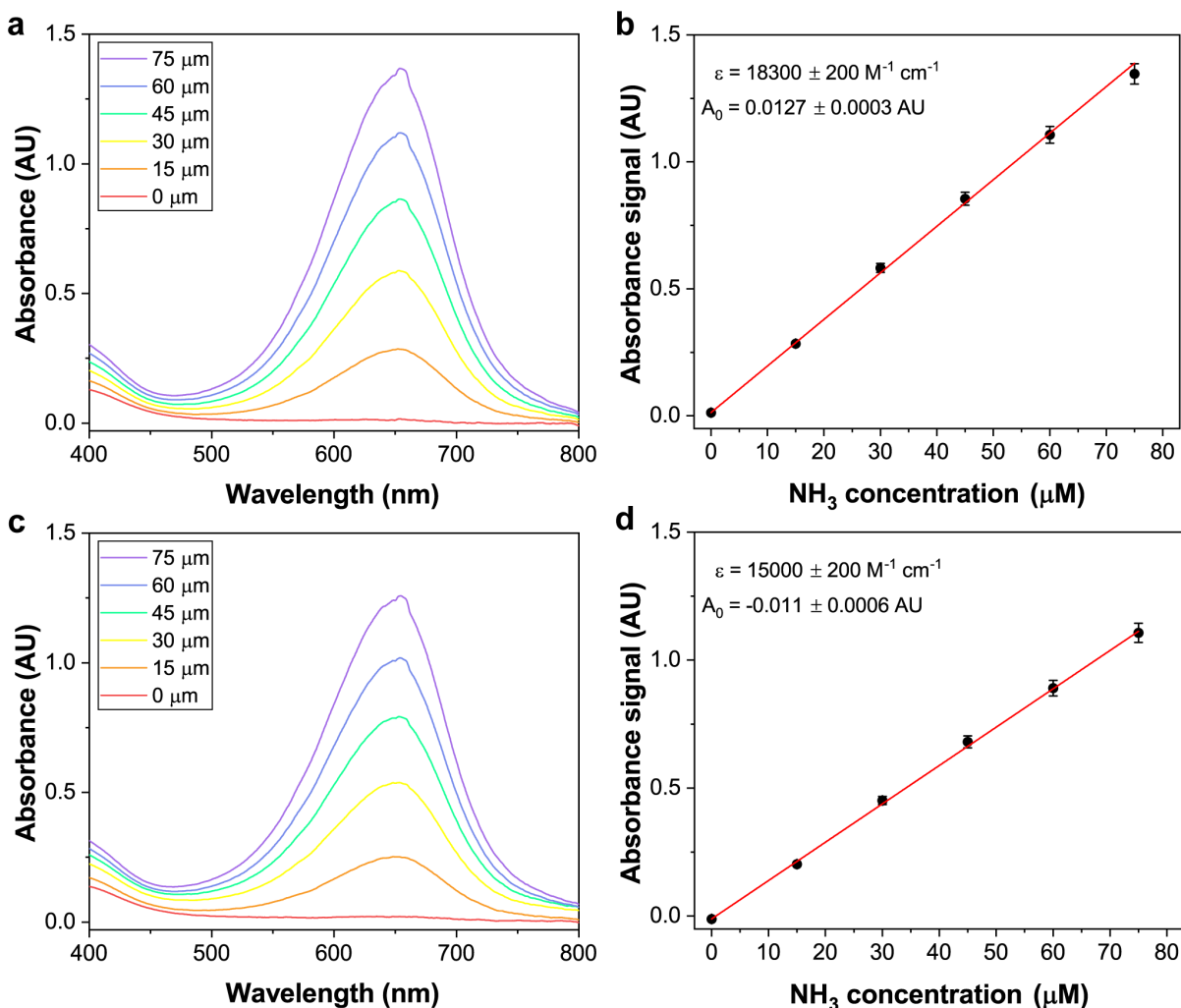


Supplementary Fig. 17. Pressure control setup used in gas diffusion electrode experiments.

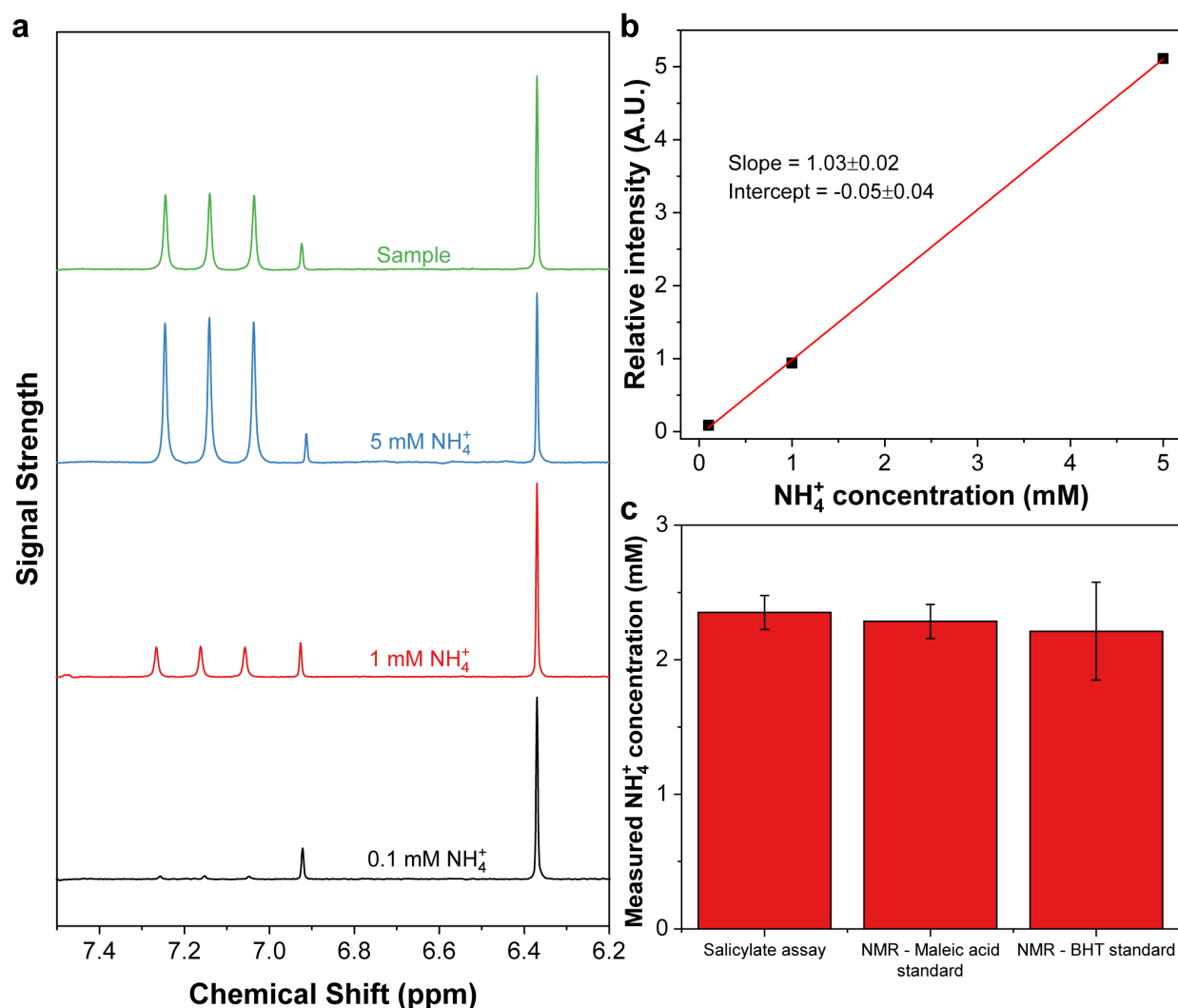
(a) Prior to addition of electrolyte to cell, no pressure gradient across the GDE/SSC is observed as gas is passed through the GDE/SSC. (b) Following addition of electrolyte, the pressure in the gas compartment increases until the pressure gradient across the GDE/SSC reaches the Laplace pressure, after which gas continues to pass through the GDE/SSC. (c) The pressure in the gas compartment is lowered, and gas begins to flow past the GDE, while the electrolyte stays in the working compartment. (d) In NRR experiments, a boric acid trap between the gas compartment and burette is added to capture gas phase ammonia.



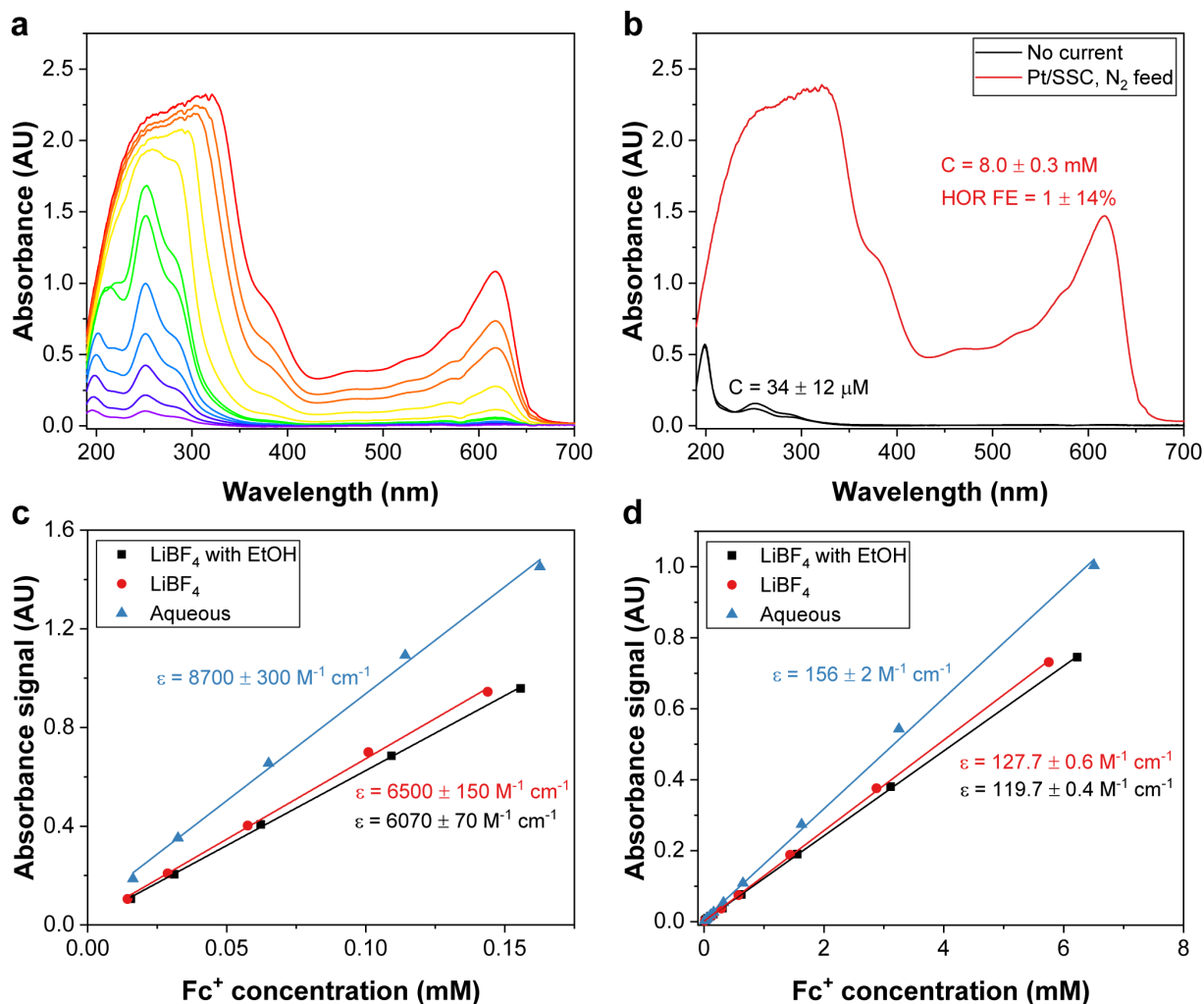
Supplementary Fig. 18. Absorbance spectra of diluted samples assayed by the salicylate method. Calibration absorbance spectra for solutions containing 0 and 60 μM of ammonia are shown. The absorbance spectra of catholyte diluted to 100 mL and further diluted 2- and 4-fold, as described in the methods, are shown. The measured ammonia concentrations of the diluted solutions are given explicitly, while the average concentration assumes that the concentrations were multiplied by their respective dilutions. The experiment was chosen at random; in this experiment, 15 mA of current were applied for a total of 7.2 coulombs of charge, N_2 was flowed past an SSC electrode in a 3-compartment cell at 10 sccm, and the pressure gradient across the SSC was 1.5 kPa. The results of this experiment can be found on data line 9 of Supplementary Table 5.



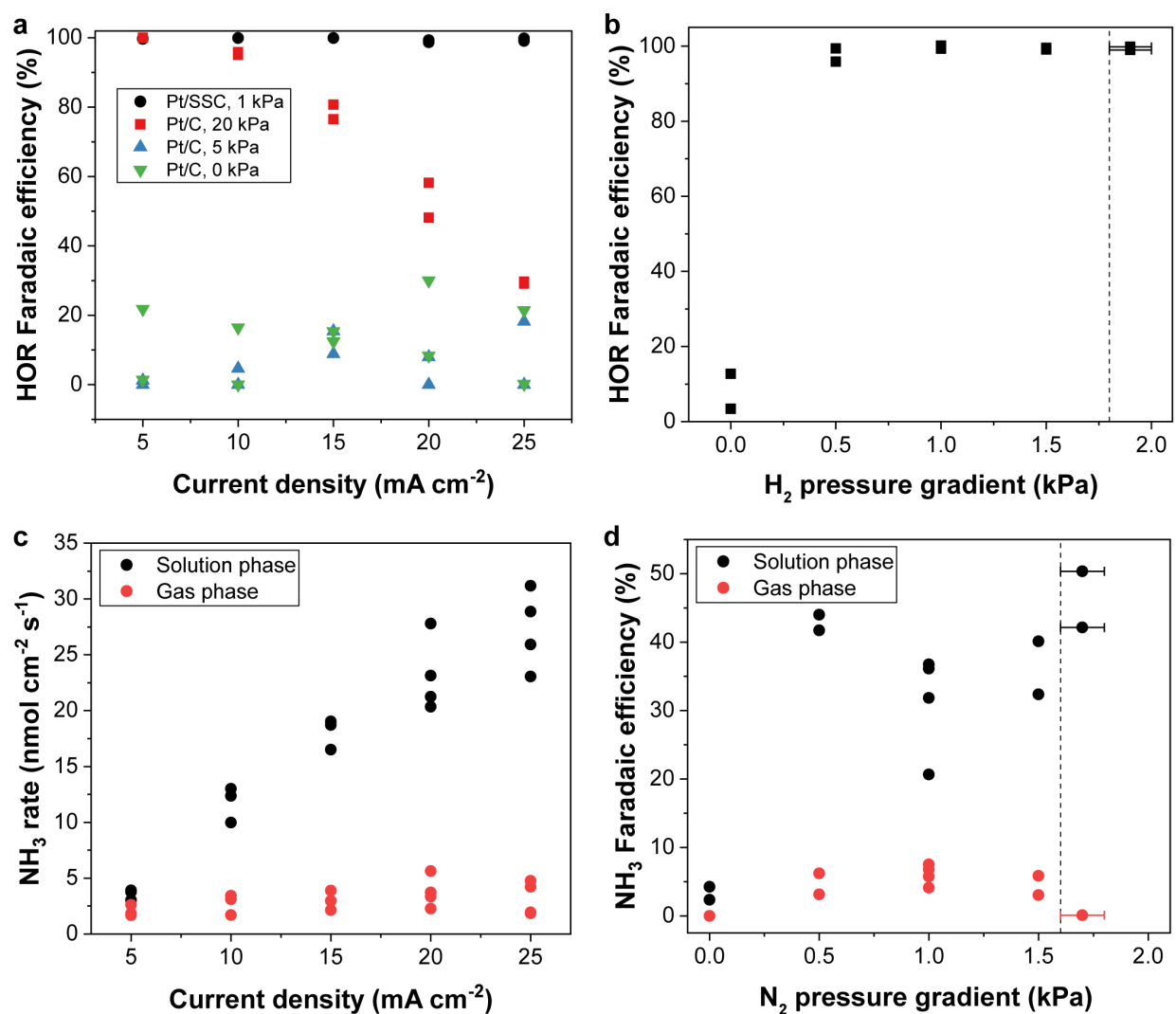
Supplementary Fig. 19. Typical calibration curves for quantifying ammonia using the indophenol method. Note that the difference between the absorbance at 650 nm and 475 nm, called the absorbance signal, is used to make the calibration curves. **(a)** Absorbance spectra for various concentrations of NH_3 in pure water. **(b)** The resulting calibration curve for NH_3 in pure water. **(c)** Absorbance spectra for various concentrations of NH_3 in water containing 5% of 1 M LiBF_4/THF electrolyte by volume. **(d)** The resulting calibration curve for NH_3 in water containing 5% v/v 1 M LiBF_4/THF electrolyte. Vertical error bars in **(b, d)** denote the standard deviation in absorbance measured between two solutions of equal concentration. Horizontal error bars in **(b, d)** denote the uncertainty in ammonia concentration when preparing solutions. Note that the effective extinction coefficient is lower in the presence of electrolyte than in pure water; the ammonia concentration is typically underestimated because the pure water calibration curve is used while samples contain some electrolyte.



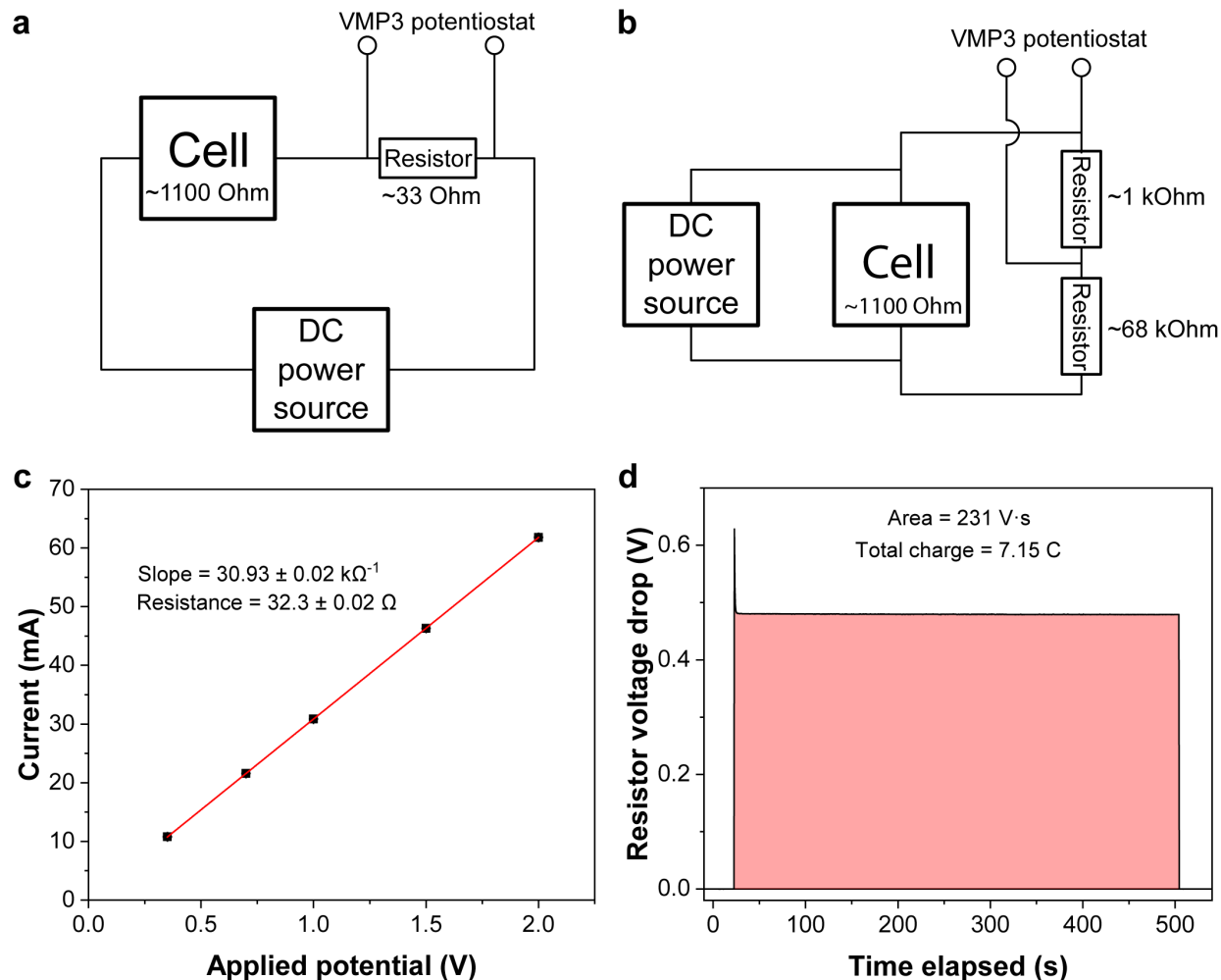
Supplementary Fig. 20. Comparison of NMR and the salicylate assay for ammonia quantification. (a) NMR spectra of 3 ammonia calibration solutions with varied NH₄⁺ concentrations in simulated acidified electrolyte (1.75 mL of 1 M LiBF₄/0.11 M EtOH/THF electrolyte, diluted to 4 mL with 0.05 M H₂SO₄) and a sample of unknown concentration with 1 mM maleic acid as an internal standard. The spectra were referenced to the maleic acid peak, which was chosen to have a chemical shift of 6.37 ppm. The solution of unknown concentration was obtained by running applying 15 mA to a 3-compartment cell with an SSC cathode through which 10 sccm of N₂ were flowed. (b) The relative peak areas of the NH₄⁺ peaks and the maleic acid peak. (c) Measured ammonia concentrations via the salicylate assay and the relative intensities of NMR peaks. The measured concentrations from the two methods are practically identical if maleic acid is used as an internal standard. Using BHT in the THF as the internal standard predicts slightly lower concentrations with large error, likely due to the smaller concentration of BHT protons in the sample solutions.



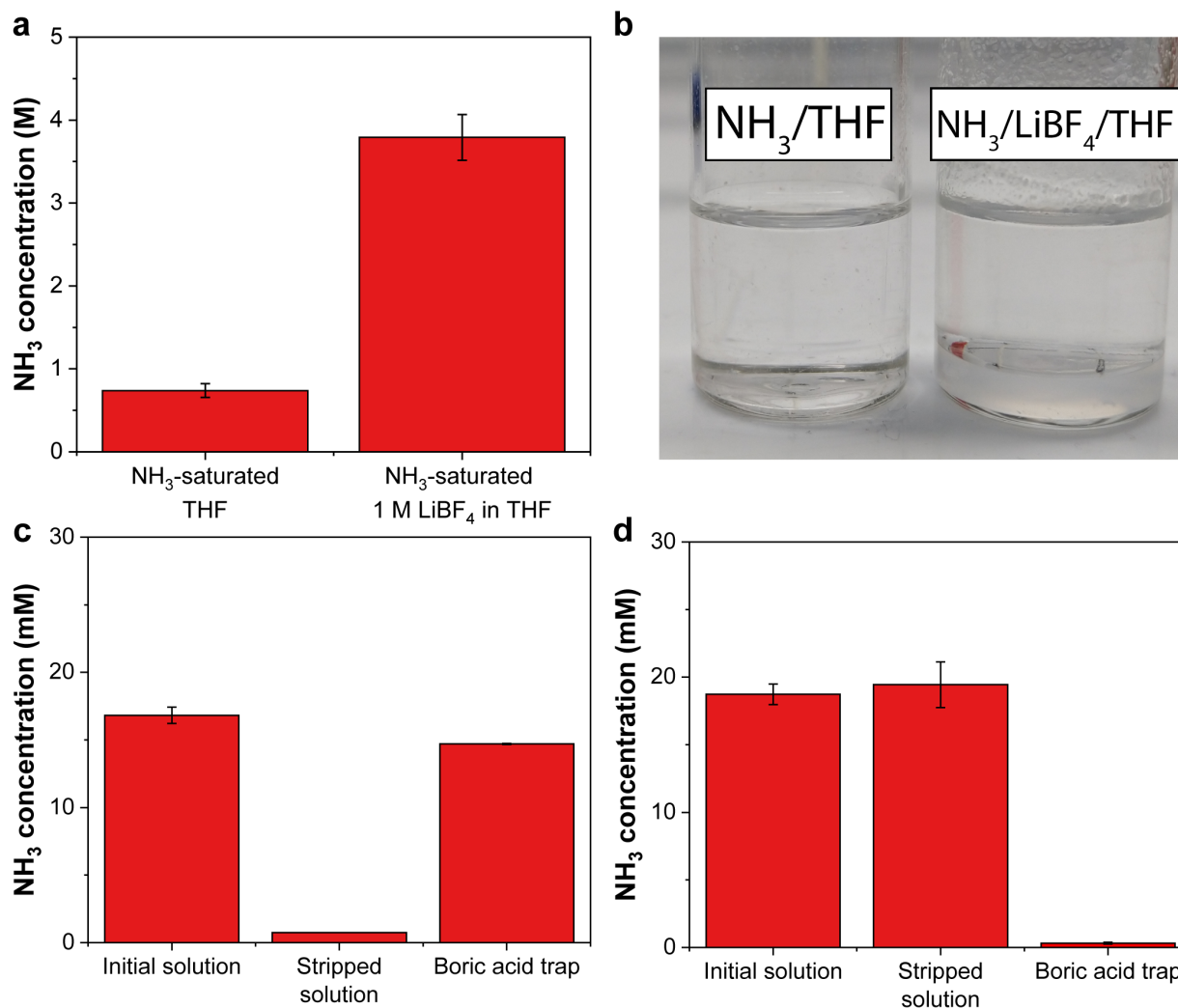
Supplementary Fig. 21. Ferrocenium calibration curves for quantifying HOR Faradaic efficiency. (a) Absorbance spectra for solutions of ferrocenium in water at a range of concentrations. (b) Absorbance spectra obtained for solutions involved in HOR control experiments. One control experiment involved using N₂ instead of H₂ as the feed gas, while the others involved applying no current for the duration of the experiment. (c) Calibration curves for the 255 nm ferrocenium signal using differently prepared solutions. (d) Calibration curves for the 619 nm ferrocenium signal using differently prepared solutions.



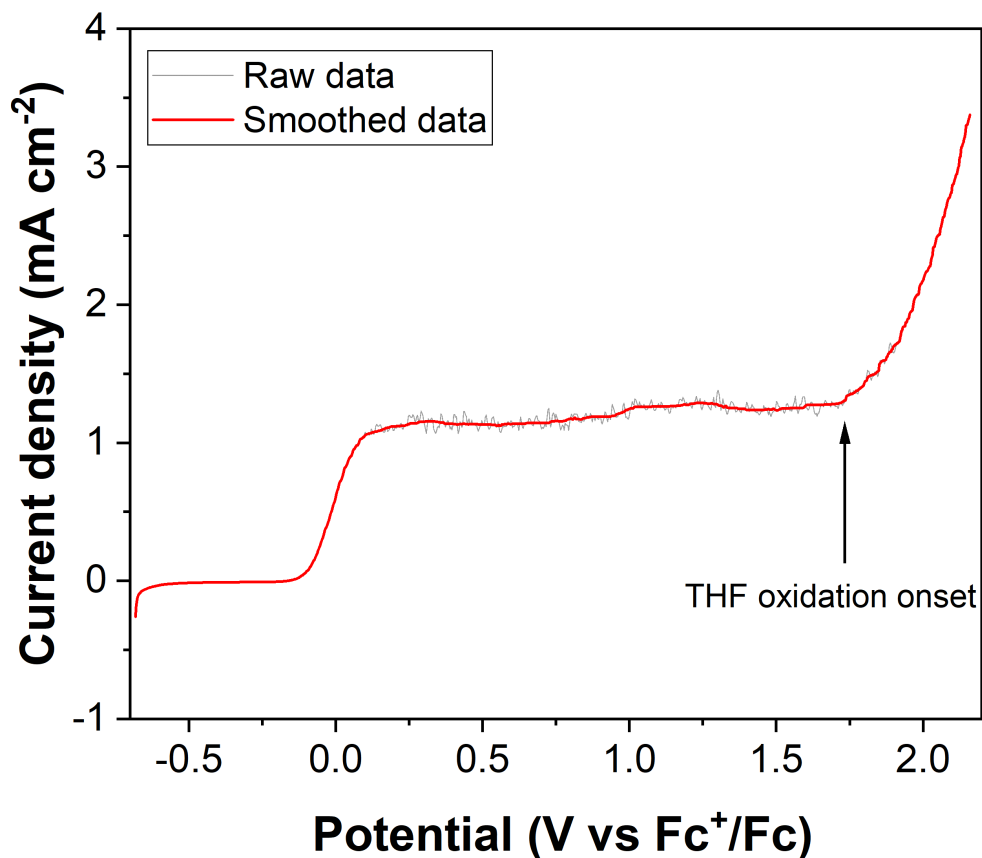
Supplementary Fig. 22. Efficiency of the steel cloth-based GDEs for HOR and NRR with raw data shown. (a) Comparison of HOR Faradaic efficiency (FE) of Pt-coated steel cloths (Pt/SSC) and Pt-loaded carbon papers (Pt/C) in various configurations. (b) Effect of pressure gradient across a Pt/SSC on HOR FE at 25 mA cm⁻² applied current density. (c) Production rate of ammonia as a function of applied current density on steel cloth cathodes at pressure gradient of 1 kPa across the steel cloth. Solution phase ammonia is found in the electrolyte while gas phase ammonia in the acid trap after the cell. (d) Effect of pressure gradient across a steel cloth cathode on FE toward NH₃ at 15 mA cm⁻² applied current density. Horizontal error bars in (b) and (d) represent the range of pressure gradient values required for gas flow through the SSCs. The dashed lines in (b) and (d) represent the onset of gas breakthrough in the SSC, which is the Laplace pressure. In all experiments, 7.2 coulombs of charge were passed to measure HOR or NRR FE.



Supplementary Fig. 23. Methods used to obtain accurate current and potential measurements when using a Tekpower DC power source. (a) Schematic of a circuit to measure current and charge passed. This scheme was used to quantify the charge passed in all experiments. **(b)** Schematic of a circuit to safely measure and record the total potential applied to the cell. This scheme was never actually used to record the potential, as the DC power source has a digital voltage readout (Fig. 4d) **(c)** A typical calibration of a resistor resistance using a VMP3 potentiostat. **(d)** An example measurement of the voltage drop across the resistor in a 15 mA NRR experiment and the resulting charge passed. As $Q = \int I dt$ and $I = V/R$, $Q = \frac{1}{R} \int V dt = \frac{231 \text{ V}\cdot\text{s}}{32.3 \text{ Ohm}} = 7.15 \text{ Coulombs}$.



Supplementary Fig. 24. Evidence of strong Li⁺-NH₃ interactions. (a) Comparison of ammonia concentrations in ammonia-saturated THF and ammonia-saturated 1 M LiBF₄ in THF. (b) Visual differences between ammonia-saturated THF with and without LiBF₄. When LiBF₄ is present, the solution separates into two phases. We speculate that the two phases may be less dense ammonia-saturated THF on top and more dense [Li(NH₃)_x][BF₄] on the bottom. (c) Results of stripping ~20 mM ammonia in THF with N₂ at 10 sccm for 10 minutes. Almost all ammonia left the solution, and was caught in the 0.1 M H₃BO₃ trap. (d) Results of stripping ~20 mM ammonia in 1 M LiBF₄ in THF with N₂ at 10 sccm for 10 minutes. Little ammonia (~2%) was stripped into the trap, demonstrating the ability of LiBF₄ to prevent ammonia stripping. Vertical error bars in (a, c, d) represent the standard deviation of computed concentrations of sample solutions; the concentrations were computed by using various dilutions of the concentrated sample solutions (n ≥ 2).



Supplementary Fig. 25. Demonstration of facile ferrocene oxidation in the electrolyte. A linear sweep voltammogram (LSV) measured at a 5 mV s^{-1} sweep rate for an electrolyte containing 10 mM ferrocene, 0.11 M EtOH, 1 M LiBF₄ in THF while flowing 10 sccm of N₂ in a 2-compartment cell at a platinum anode. While thermodynamically ferrocene oxidation is preferred to THF oxidation, it is important to demonstrate that this is accurate kinetically. Here, we see that ferrocene oxidation starts to occur at potentials slightly below 0 V vs Fc⁺/Fc due to a Nernstian shift, after which it quickly reaches the transport-limited current density. THF oxidation occurs at higher potentials; the exact value of THF oxidation was found to be sensitive to platinum anode preparation and age, as well as electrolyte composition. The data were smoothed by using a 50th percentile smooth filter.

Supplementary Tables

Supplementary Table 1. Compilation of literature highest reported rates obtained in nonaqueous electrolytes at close-to-ambient conditions. The data are plotted in Fig. 4a.

Cathode material	Electrolyte	Conditions	Highest NH ₃ production rate, nmol cm ⁻² s ⁻¹	NH ₃ FE at highest rate, %	Reference
Ag-Au@ZIF	0.2 M LiCF ₃ SO ₃ , ~1% EtOH, THF	Ambient	0.010	18.0	17
Stainless steel cloth, flooded	[C ₄ mpyr][eFAP]	Ambient	0.021	34.0	18
Copper foil	1 M LiBF ₄ , 0.2 M EtOH, THF	Ambient	7.88	15.2	1
Silver foil	0.2 M LiClO ₄ , 0.18 M EtOH, THF	Ambient	0.58	8.4	19
Iron foil	0.2 M LiClO ₄ , 0.18 M EtOH, THF	50 bar N ₂ , 25 °C	3.99	57.7	
Molybdenum foil	0.2 M LiClO ₄ , 0.18 M EtOH, THF	Ambient	0.22	7.5	20
Nickel foil	0.1 M LiCl in EDA	Ambient	0.036	17.2	21
Porous nickel	0.01 M H ₂ SO ₄ in 9:1 2-propanol/water	Ambient	0.015	0.85	22
Polyaniline on platinum	0.03 M H ₂ SO ₄ , 0.1 M LiClO ₄ , MeOH	50 bar N ₂ , 25 °C	0.44	16	23
Nickel	LiClO ₄ , EtOH, THF	Ambient	0.26	3.8	24
Nickel	LiClO ₄ , THF, EtOH, PYR-14 TFSI Ionic Liquid	Ambient	0.11	1.7	
Stainless steel cloth, GDE	1 M LiBF ₄ , 0.1 M EtOH	Ambient	30.4	35.3	Present work

Supplementary Table 2. Raw data for current density variation for hydrogen oxidation on various substrates. The data are plotted in Fig. 3a.

Current density, mA cm ⁻²	Electrode/condition	Ferrocenium concentration, mM	Ferrocenium FE, %	HOR FE, %
5	Pt/C, 0 kPa	5.87	78.21	21.79
5	Pt/C, 0 kPa	7.39	98.57	1.43
10	Pt/C, 0 kPa	7.82	104.33	-4.33
10	Pt/C, 0 kPa	6.27	83.56	16.44
15	Pt/C, 0 kPa	6.57	87.57	12.43
15	Pt/C, 0 kPa	6.35	84.65	15.35
20	Pt/C, 0 kPa	6.87	91.67	8.33
20	Pt/C, 0 kPa	5.25	69.99	30.01
25	Pt/C, 0 kPa	5.90	78.62	21.38
25	Pt/C, 0 kPa	7.48	99.82	0.18
5	Pt/C 5 kPa	7.41	98.81	1.19
5	Pt/C 5 kPa	8.22	109.80	-9.80
10	Pt/C 5 kPa	8.76	116.95	-16.95
10	Pt/C 5 kPa	7.14	95.32	4.68
15	Pt/C 5 kPa	6.83	91.14	8.86
15	Pt/C 5 kPa	6.34	84.55	15.45
20	Pt/C 5 kPa	8.30	110.84	-10.84
20	Pt/C 5 kPa	6.90	92.03	7.97
25	Pt/C 5 kPa	8.26	110.33	-10.33
25	Pt/C 5 kPa	6.13	81.76	18.24
5	Pt/C 20 kPa	0.03	-0.05	100.05
5	Pt/C 20 kPa	0.03	0.00	100.00
10	Pt/C 20 kPa	0.34	4.11	95.89
10	Pt/C 20 kPa	0.40	4.95	95.05
15	Pt/C 20 kPa	1.79	23.51	76.49
15	Pt/C 20 kPa	1.47	19.25	80.75
20	Pt/C 20 kPa	3.90	51.80	48.20
20	Pt/C 20 kPa	3.15	41.83	58.17
25	Pt/C 20 kPa	5.28	70.32	29.68
25	Pt/C 20 kPa	5.32	70.88	29.12
5	Pt/SSC, 1 kPa	0.060	0.37	99.63
5	Pt/SSC, 1 kPa	0.047	0.20	99.80
10	Pt/SSC, 1 kPa	0.040	0.10	99.90
10	Pt/SSC, 1 kPa	0.035	0.03	99.97
15	Pt/SSC, 1 kPa	0.036	0.05	99.95
15	Pt/SSC, 1 kPa	0.038	0.08	99.92
20	Pt/SSC, 1 kPa	0.081	0.65	99.35
20	Pt/SSC, 1 kPa	0.129	1.30	98.70
25	Pt/SSC, 1 kPa	0.100	0.90	99.10
25	Pt/SSC, 1 kPa	0.043	0.14	99.86

Supplementary Table 3. Raw data for pressure gradient variation for hydrogen oxidation on Pt/SSC. The data are plotted in Fig. 3b.

Pressure gradient, kPa	Ferrocenium concentration, mM	Ferrocenium FE, %	HOR FE, %
0	6.54	87.28	12.72
0	7.24	96.63	3.37
0.5	0.08	0.60	99.40
0.5	0.34	4.14	95.86
1	0.02	-0.12	100.12
1	0.08	0.65	99.35
1.5	0.07	0.49	99.51
1.5	0.10	0.90	99.10
1.9	0.05	0.21	99.79
1.9	0.11	1.01	98.99

Supplementary Table 4. Raw data for current density variation for nitrogen reduction on steel cloths. The data are plotted in Fig. 3c.

Current density, mA cm ⁻²	NH ₃ solution FE, %	NH ₃ gas FE, %	NH ₃ total FE, %	NH ₃ solution rate, nmol cm ⁻² s ⁻¹	NH ₃ gas rate, nmol cm ⁻² s ⁻¹	NH ₃ total rate, nmol cm ⁻² s ⁻¹
5	22.59	9.65	32.25	3.90	1.67	5.57
5	17.51	10.58	28.09	3.02	1.83	4.85
5	21.78	15.15	36.92	3.76	2.62	6.38
10	28.88	4.92	33.81	9.98	1.70	11.68
10	37.66	9.94	47.60	13.01	3.43	16.44
10	35.80	9.01	44.81	12.37	3.11	15.48
15	36.13	7.50	43.63	18.72	3.89	22.61
15	36.74	4.10	40.84	19.03	2.12	21.16
15	31.84	5.74	37.58	16.50	2.98	19.47
20	30.76	5.38	36.14	21.25	3.71	24.97
20	40.23	4.85	45.07	27.79	3.35	31.14
20	29.46	3.27	32.74	20.35	2.26	22.62
20	33.47	8.14	41.62	23.13	5.62	28.75
25	36.09	5.52	41.61	31.17	4.76	35.93
25	33.43	4.88	38.31	28.87	4.22	33.09
25	26.70	2.25	28.94	23.05	1.94	24.99
25	30.01	2.14	32.15	25.92	1.85	27.77

Supplementary Table 5. Raw data for pressure gradient variation across the electrode for nitrogen reduction on steel cloths. The data are plotted in Fig. 3d.

Pressure gradient, kPa	NH ₃ solution FE, %	NH ₃ gas FE, %	Total FE, %	NH ₃ solution rate, nmol cm ⁻² s ⁻¹	NH ₃ gas rate, nmol cm ⁻² s ⁻¹	NH ₃ total rate, nmol cm ⁻² s ⁻¹
0	2.32	-	2.32	1.20	-	1.20
0	4.22	-	4.22	2.19	-	2.19
0.5	44.00	6.20	50.20	22.80	3.21	26.01
0.5	41.72	3.12	44.84	21.62	1.62	23.24
1.0	20.67	6.74	27.41	10.71	3.49	14.20
1.0	36.13	7.50	43.63	18.72	3.89	22.61
1.0	36.74	4.10	40.84	19.03	2.12	21.16
1.5	31.84	5.74	37.58	16.50	2.98	19.47
1.5	32.36	5.85	38.21	16.77	3.03	19.80
1.7	40.11	3.01	43.12	20.78	1.56	22.34
1.7	42.15	0.09	42.25	27.93	0.08	28.01

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