

Supplementary materials

Membrane electrode assembly design for lithium-mediated electrochemical nitrogen reduction

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Methods

Materials

Tetrahydrofuran (THF, $\geq 99.9\%$, inhibitor-free), lithium tetrafluoroborate (LiBF_4 , 98%), potassium hydroxide (KOH, $\geq 85\%$), polyethylene oxide (PEO, $M_v \sim 300,000$), lithium ethoxide ($\text{CH}_3\text{CH}_2\text{OLi}$, 95%) and isotope labelled nitrogen ($^{15}\text{N}_2$, 98 atom% ^{15}N) were purchased from Sigma-Aldrich. Ammonium chloride (NH_4Cl , PT), salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$, 99.5%) and sodium nitroferricyanide dihydrate ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$, 99%) were purchased from Aladdin. Sulfuric acid (H_2SO_4 , 95~98%) and trisodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Steel cloth (304 stainless-steel, 400X400 mesh) was purchased from Golden Bug Flagship Store. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5%, Water ≤ 50 ppm) was obtained from Adamas. Molecular sieves (4 Å, 3.2 mm diameter) were purchased from Acros Organics. Sodium hypochlorite (NaClO , $\geq 7.5\%$) was purchased from General-Reagent. Pt/C (TEC10V30E, 30 wt%) was obtained from Tanaka. Nafion solution (20 wt%) were purchased from Hesen. Ultra-high purity nitrogen (N_2 , 99.999%) and argon (Ar, 99.999%) were purchased from Likang Gas, Shanghai. Ultra-high purity hydrogen (99.999%, H_2) was provided by Air Liquide, Shanghai.

Synthesis of PEO membrane

Before synthesis process, LiBF_4 was vacuum-dried at 110°C for 12 hours to remove the potential water. Then, PEO powder was added into THF at concentration of 60 mg mL^{-1} . The mixture was stirred at 40°C until homogeneous solution was obtained. Subsequently, LiBF_4 and EtOLi were added into PEO solution with molar ratio of 6:1 (EO: LiBF_4) and 12:1 (EO:EtOLi), respectively. And the mixture was stirred at 35°C for another 2 hours, during which the solution become transparent and uniform. The water content of membrane solution was estimated to be 16.4 ± 2.4 ppm via Karl Fisher method by three independent tests. Finally, the as-prepared solution was casted onto a dish Teflon and dried for 24 hours at room temperature in glovebox filled with Ar (Fig. S1).

Preparation of electrodes

Lithium deposited stainless-steel cloth (Li-SS cloth) was employed as working electrode in electrochemical ammonia synthesis. Typically, stainless-steel (SS) cloth was assembled in a sealed cell with its one side exposed to THF solution containing 1 M LiBF_4 (Fig. S4). The area of lithium deposition was precisely limited to $1 \times 1\text{ cm}^2$ realized by attaching a hollow PTFE border on SS cloth. Lithium plating was carried out by performing chronopotentiometry at $-5\text{ mA cm}_{\text{geo}}^{-2}$ for 3000 s (Fig. S5). After deposition, Li-SS cloth was taken out of deposition cell and employed as anode for assembly of NRR electrolytic cell. The undeposited area of the SS cloth was cut away.

All operations were conducted in glovebox except electrochemical measurements.

Carbon paper loaded with Pt/C catalysis was adopted for hydrogen oxidation reaction (HOR) at anode. Typically, 8 mg Pt/C catalysts was dispersed in 800 μL of absolute alcohol, followed by addition of 40 μL of 5% Nafion solution. To obtain a uniform ink, the mixture was sonicated for 1 hour. Finally, 105 μL of the uniform ink was dropped on $1 \times 1\text{ cm}^2$ carbon paper with loading of approximate $1\text{ mg}_{\text{cat}}\text{ cm}^{-2}$. The as-prepared electrode was cleaned

by consecutive cyclic voltammetry scans introduced in our previous work¹, followed by vacuum-dried at 65 °C before use.

Material characterizations

X-ray diffraction patterns (XRD) of PEO membranes were garnered using an X-ray diffractometer (Rigaku Mini Flex 600) with Cu K α radiation. To avoid the interference of moisture in air, membrane sample was covered by polyimide tape on glass sheet (Fig. S3). In-situ XRD data was collected by a Bruker D8 Advance in situ X-ray diffractometer with Cu K α radiation. The real time XRD pattern collection during electrolysis was realized by a home-made electrolytic cell (Fig. 7C). In-situ XRD test followed the identical procedure as regular test, which is introduced in electrochemical measurements section.

The morphology/energy dispersive spectroscopy (EDS) of membrane electrode assembly (MEA) was obtained by a JEOL JSM-7800F scanning electron microscope operating at 10.0 kV. The near surface chemical state of samples was examined by X-ray photoelectron spectroscopy (NEXSA, Thermo Fisher Scientific) with the monochromatic Al K α X-ray as the X-ray source. The near surface composition was revealed by time-of-flight secondary ion mass spectrometry (TOF-SIMS 5-100, ION-TOF GmbH). The analysis was carried out with Bi³⁺ primary ions at 30 keV in negative mode. Maps consisting of 256 pixels X 256 pixels covering the same field of 150 X 150 μm^2 area were collected with the pixel resolution of 0.59 μm in both x and y direction. The element information in bulk (well beneath the surface) was collected by time-of-flight secondary ion mass spectrometry coupled with focused ion beam (FIB-ToF-SIMS, GAIA3, TESCAN, Gallium ion source). The acquisition was conducted at the ion beam energy and current density of 30 keV and 1 nA in positive mode. Sputtering was focused on region of 10.4 X 10.4 μm^2 , with resolution of 600 X 600 pixels. FIB realized material removal by mechanical sputtering and ionization. During the test, the material was sputtered away frame by frame, while the secondary ions were generated, extracted and passed through the TOF-SIMS analyser, producing mass spectra for each point in the map.

All The samples were prepared and preserved in glovebox filled with Ar. For XPS measurements, the sample was transported from the glovebox to the XPS via a gas tight suitcase to avoid any exposure to air.

Gas circuit setup

Configuration of entire gas circuit was illustrated in Fig. S8. Nitrogen and hydrogen gas were used as feed gas for cathode and anode, respectively. Basically, the gas circuit mainly consists of two parts: gas pretreatment and an acid trap.

Before the gas passed into the cell, it needed to go through several gas washing bottle. The cathode side consists of three consecutive bottles, including a bottle containing 0.05 M H₂SO₄ and a bottle containing 0.1 M KOH to remove alkaline and acidic N-containing impurities respectively,^{2,3} a bottle filled with THF solution mixed with dried molecular sieves to remove water. A PTFE water filter was placed in front of the THF cylinder to block most of the water vapor in advance. The configuration of gas pretreatment part at anode side is almost the same as cathode side except that an additional bottle was set to provide certain amount of ethanol in feed gas.

Downstream of the electrolytic cell, there was an acid trap at cathode side, which was capable of absorbing produced ammonia in tail gas. While the anodic side was not equipped with acid trap in most case because little ammonia was detected in anodic acid trap (Fig. S13). A measuring cylinder filled with water was placed at the end of gas circuit to absorb THF and monitor gas flow rate.

Electrochemical measurements

Oxygen and moisture in air will induce deterioration of Li-SS cloth and have negative impacts on electrochemical measurements and material characterizations. It should be pointed out that the effect of air can't be totally eliminated since electrochemical measurements were conducted outside the glovebox. But its negative impact could be minimized by adopting the following procedures.

Before the test, gas diffusion electrolytic cell for NRR was assembled in glovebox, where water and oxygen content in glovebox were both strictly constrained below 0.1 ppm. The inlet and outlet of cell were blocked with stoppers to avoid the entry of air during transfer. Then, the completed electrolytic cell was sealed in plastic bag and taken out of glovebox. Before the cell was connected into gas circuit, 5 standard cubic centimeters per minute (sccm) of feed gas were bubbled through the entire setup for at least 10 minutes, removing the residual air in pipeline. Next, we took the cell out of plastic bag, removed the stopper and connected it into gas circuit in a very short time. Gas flow went through the gas diffusion electrolytic cell for another 1 hour at rate of 2 sccm, during which, the MEA inside was fully humidified. Then, certain ethanol was injected into THF gas-washing bottle at anode by an injection syringe. Electrochemical measurements were performed using Gamry Reference 3000 electrochemical workstation. The electrolysis was performed at constant cell voltage for 4 hours, sometimes followed immediately by open circuit potential test.

After test, the MEA, including anode, PEO membrane and cathode) was taken out of electrolytic cell for further measurement. The remaining components went through careful rinses by ethanol wiping and ultrasonic cleaning, followed by rinsing with Milli-Q water. Finally, they were transferred to oven and dried at 75 °C under vacuum for overnight before next use.

¹⁵N₂ isotopic experiments

The ¹⁵N₂ isotopic tests were performed following the same protocol as that of normal tests introduced above except that there were some modifications in procedure of feeding gases. Firstly, Ar was utilized as feed gas to wipe out the residual air in pipeline. The ventilation rate was maintained at 5 sccm for 10 minutes. Then, electrolytic cell was connected into the gas circuit. And the feed gas was switched from Ar to ¹⁵N₂ quickly and kept unchanged throughout the whole electrochemical test.

Ammonia quantification

After electrochemical test, fixed nitrogen was determined by considering products in MEA and tail gas absorber. To dissolve the ammonia and other intermediate products (lithium amide, lithium imide, etc) in MEA, MEA was immersed in 5 mL of 0.1 M H₂SO₄ for

at least 1 hour during which all nitrogen containing products were converted to ammonia. It should be noted that the tail gas absorber itself provides an acidic environment (0.1 M H₂SO₄) for ammonia conversion so that additional acidification is not necessary here.

Further, ammonia concentration in solution sample was quantified by a modified indophenol blue method. Typically, 0.1 mL of samples was mixed with 1 mL of 1 M NaOH solution containing 5 wt.% salicylic acid and 5 wt.% sodium citrate. Then, 0.5 mL of 0.05 M NaClO solution, 0.1 mL of aqueous solution of 1 wt.% sodium nitroferricyanide and 0.9 mL Milli-Q water were added in sequence. After 1 hour of color development, the absorption spectrum (background correction by blank solution included) was obtained using UV-Vis spectrophotometer (Mapada, P4). Finally, ammonia concentration was determined by substituting absorption value at 655 nm into calibration curve (Fig. S14).

Besides indophenol blue method, nuclear magnetic resonance (NMR) measurement was also employed to quantify ¹⁵NH₃ products in ¹⁵N₂ isotopic test so that ammonia synthesis by nitrogen reduction can be fully validated. In our NMR measurements, maleic acid and DMSO-d₆ were utilized as internal standard and deuterium reagent, correspondingly. Following a typical procedure, 150 μL of sample solution was amalgamated with 25 μL of 3 mM maleic acid solution (10 vol.% H₂O +90% vol.% DMSO-d₆) and 575 μL of DMSO-d₆, resulting in a total volume of 750 μL. The as-prepared solution was then sealed in a nuclear magnetic tube and analyzed using a Bruker AVANCE NEO spectrometer operating at a ¹H frequency of 700.23 MHz. The spectrum was acquired using the zg30 program with 256 scans.

Gas purity analysis

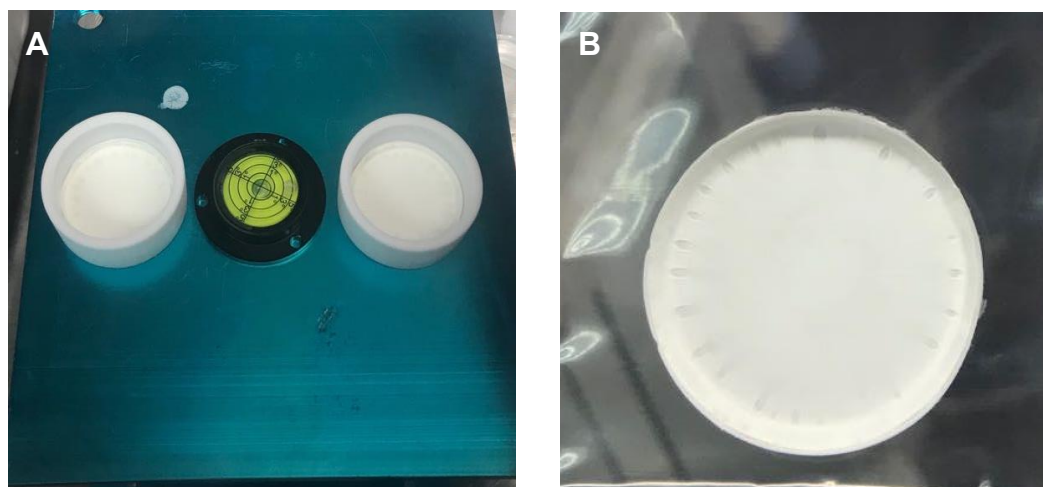
To avoid false positive results, possible nitrogen-containing contaminants in feed gases (N₂, ¹⁵N₂ and H₂) were evaluated, as suggested by literature.^{2, 4} NH₃ and NO_x compounds in gas flow were captured by gas traps containing 0.05 M H₂SO₄ and 0.1 M KOH, respectively. The bubbling rate was kept at 2 sccm for 4 hours, which was the same as that for electrolysis. Then, ammonia, nitrite and nitrate in absorption solution were quantified by UV-Vis spectrophotometry after addition of specific indicator.

Ammonia was quantified followed the same procedure as introduced in “**Ammonia quantification**” section, except that we increased the sample amount to 0.5 mL to realize better sensitivity.

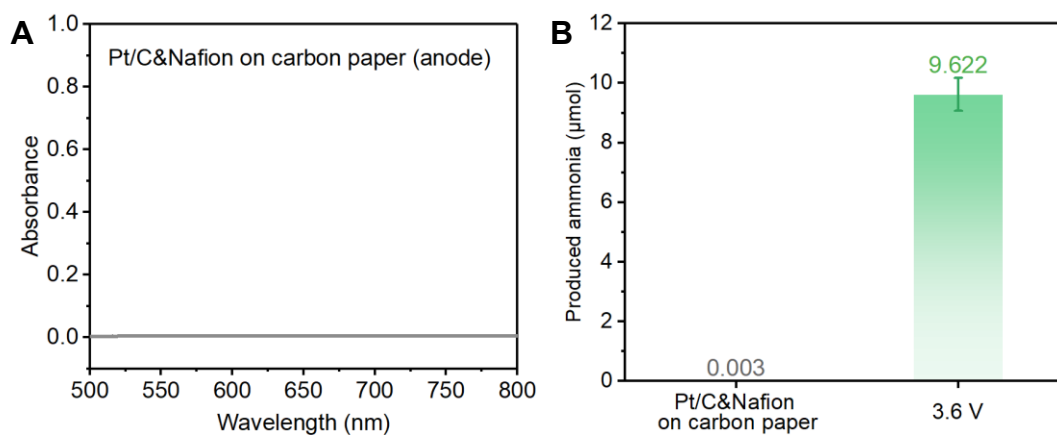
For the NO₂⁻ analysis, 1 mL of samples was acidified by 1 mL 0.1 M H₂SO₄, followed by addition of 0.5 mL of Milli-Q water and 0.1 mL of Griess indicator. Absorption spectrum was acquired after 1 hour. The Griess indicator was prepared by dissolving 2 g of p-aminobenzenesulfonamide, 0.1 g of N-(1-naphthyl)-ethylenediamine dihydrochloride and 5 mL of phosphoric acid in 50 mL of Milli-Q water.

For the NO₃⁻ analysis, 0.4 mL of samples was acidified by 0.8 mL of 0.1 M HCl, followed by addition of 0.8 mL of ammonium sulfamate solution with concentration of 12.5 g mL⁻¹ and 2.8 mL of Milli-Q water. The solution was incubated for 30 min before absorption spectrum was acquired.

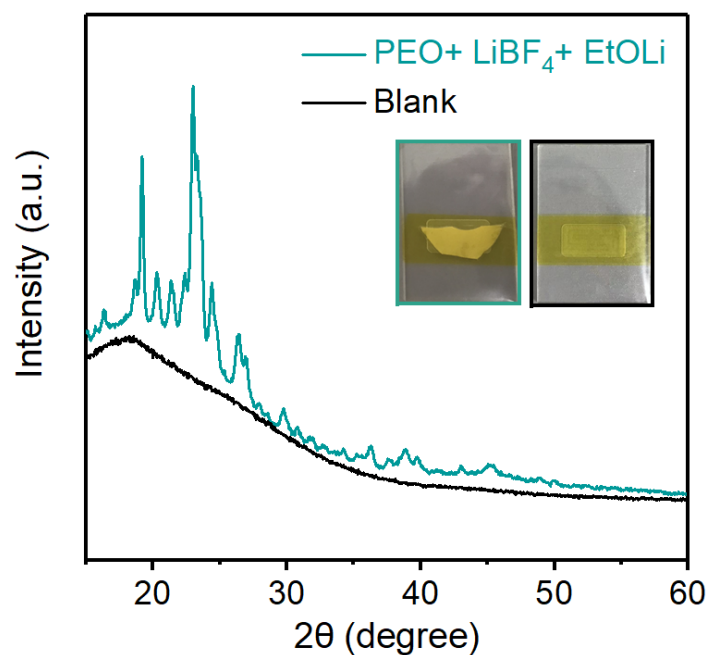
Supplementary Figures



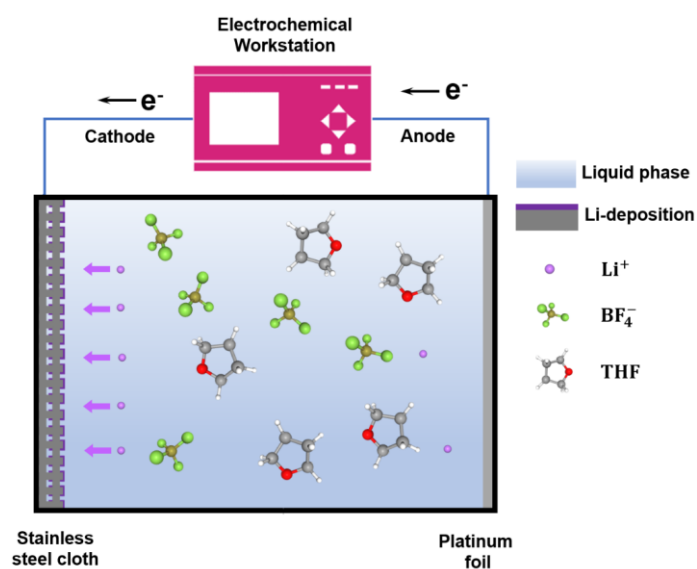
Supplementary Fig. S1. Photographs of as-prepared PEO membrane. (A) PEO membranes were volatilizing solvent in PTFE dishes. (B) After complete evaporation, PEO membranes were stripped from PTFE dishes and restored in glovebox.



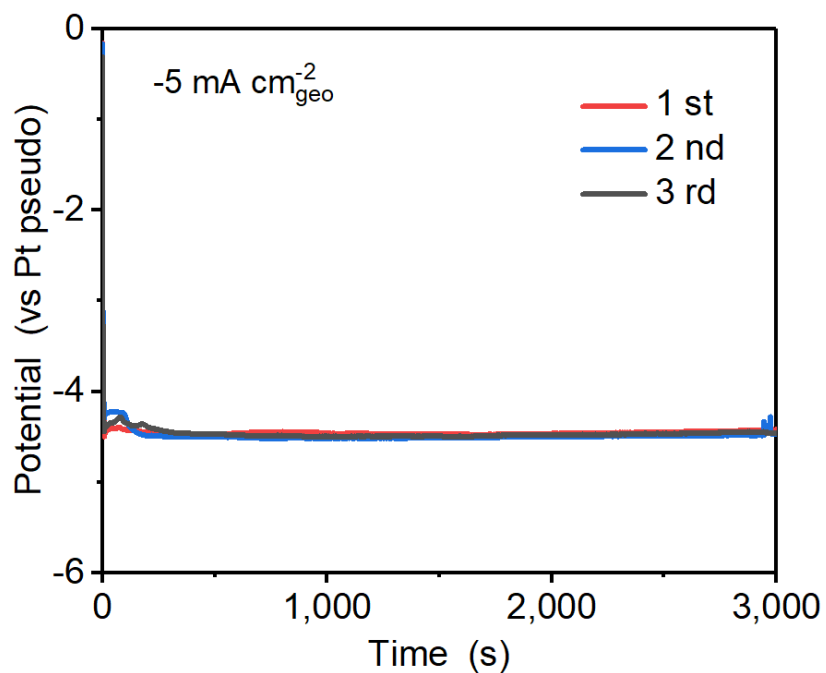
Supplementary Fig. S2. (A) UV/Vis spectra of sample solution stained with indophenol blue indicator. (B) Comparison of ammonia detected in anode and in a typical electrochemical test.



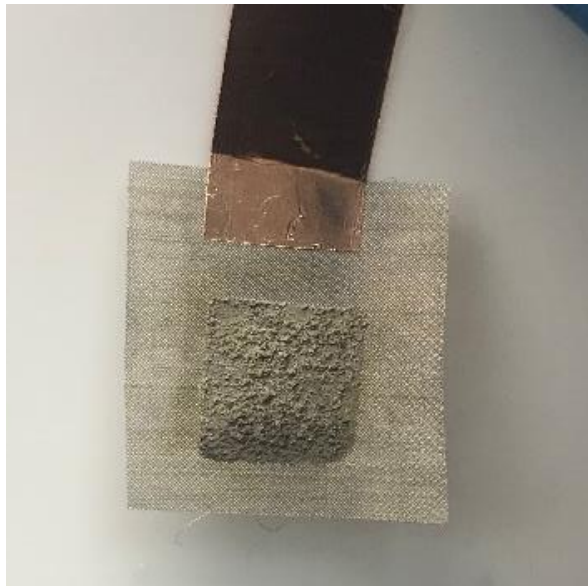
Supplementary Fig. S3. Comparison of XRD patterns between PEO membrane and blank. To avoid the interference of moisture in air, membrane sample was covered by polyimide tape on glass sheet (insets above).



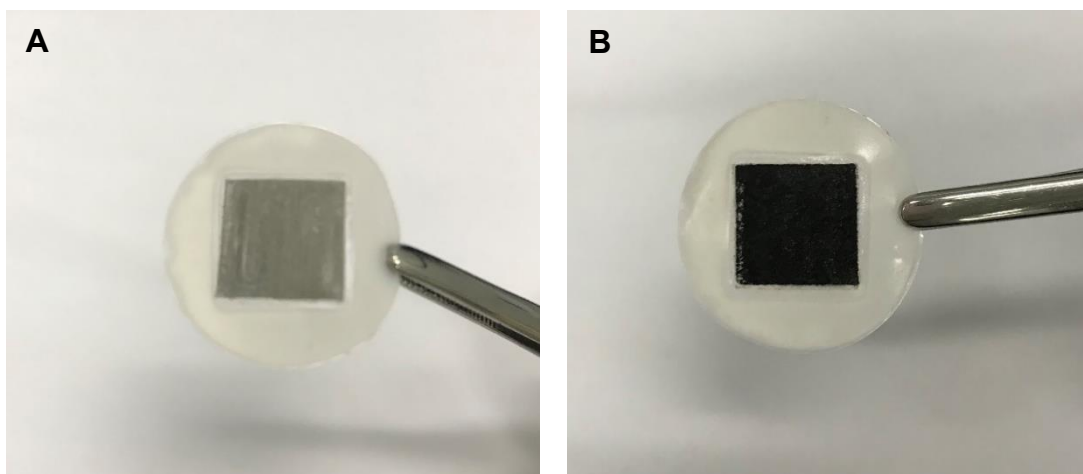
Supplementary Fig. S4. Schematic of closed electrolytic cell for lithium deposition. The cell was assembled and injected with electrolyte in glovebox filled with Ar. Then, the cell was well sealed and moved out of glovebox for electrochemical measurements.



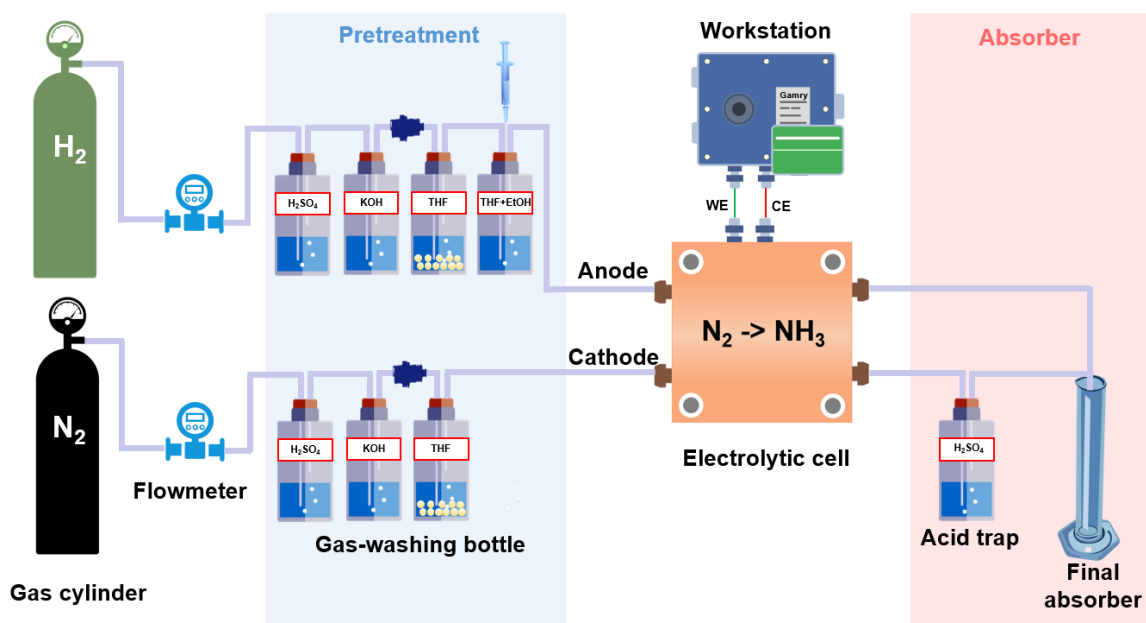
Supplementary Fig. S5. Lithium plating on SS cloth at current density of $-5 \text{ mA cm}_{\text{geo}}^{-2}$. Potential curves show good consistency from three independent measurements.



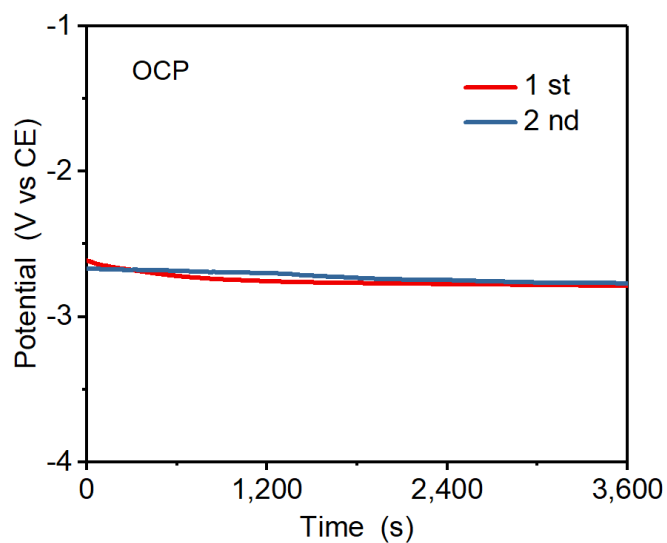
Supplementary Fig. S6. Photograph of Li-SS cloth with lithium deposits in $1 \times 1 \text{ cm}^2$ area.



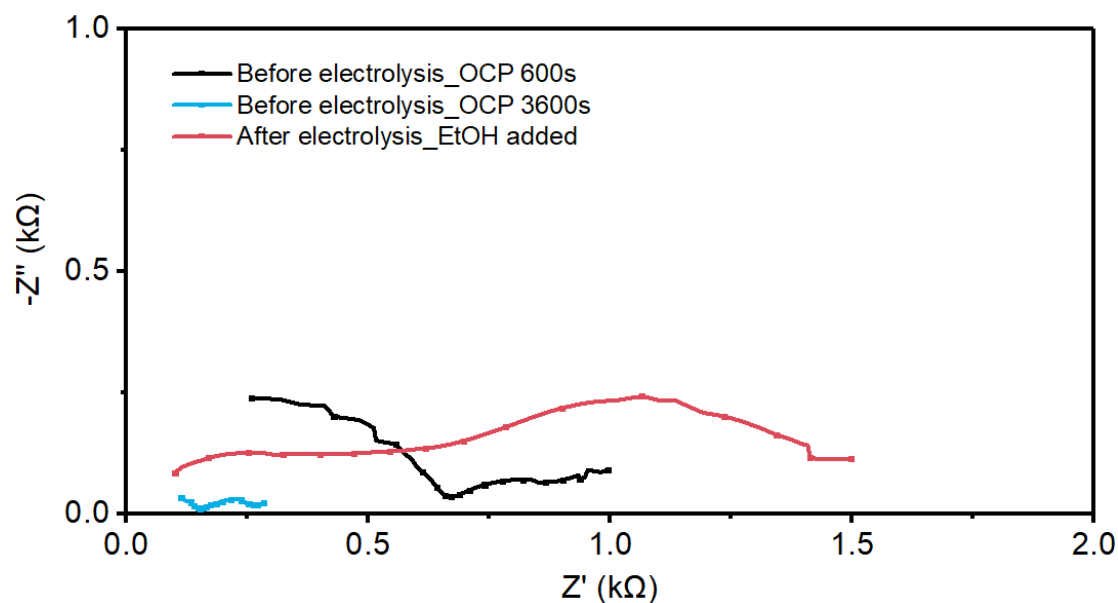
Supplementary Fig. S7. Photographs of MEA from (A) cathode side and (B) anode side.



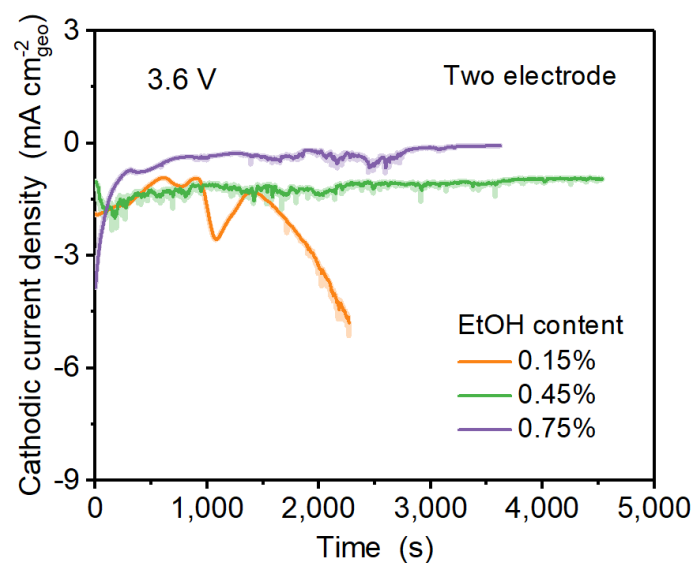
Supplementary Fig. S8 Schematic of gas circuit setup in experiments. Fed gas was purified and humidified by gas-washing bottles before conducting to the cell. And the tail gas was delivered into an acid trap to capture the ammonia in gas phase.



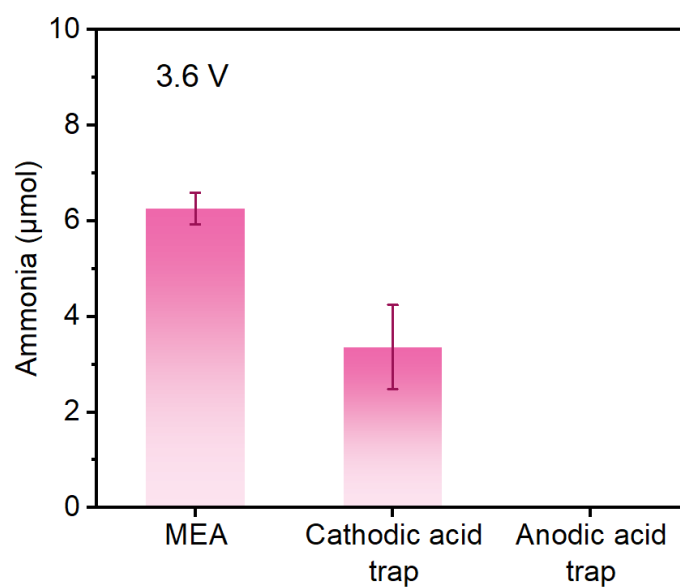
Supplementary Fig. 10. Open circuit potential test before chrono-amperometric measurements. The cathode side and anode side were fed with N_2 and H_2 , respectively. The potential was more positive than equilibrium potential between metallic lithium and hydrogen oxidation reaction, which was estimated by immediate open circuit test after electrolysis (Fig. S23). We suppose that could be attributed to lower shift of anode potential induced by alkaline EtOLi.



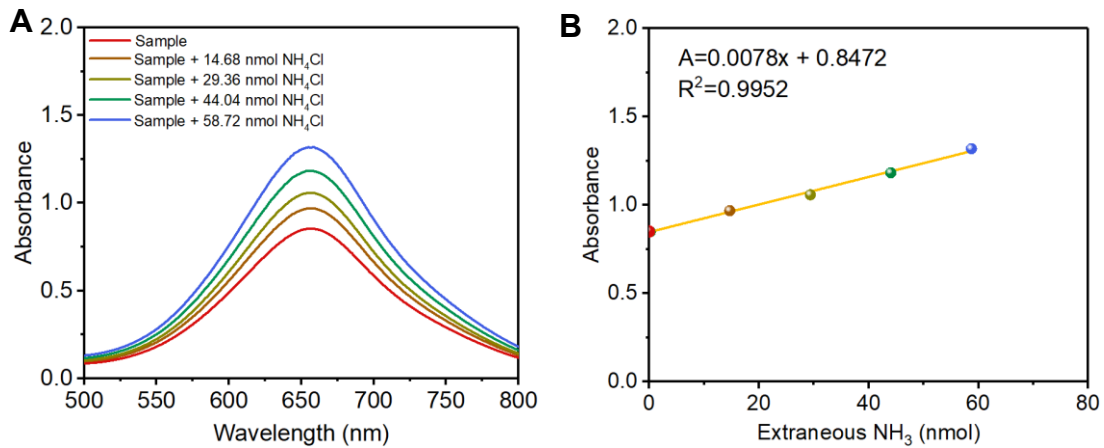
Supplementary Fig. S11. Typical electrochemical impedance spectroscopy profiles at different stages of experiments. EIS data was plotted for every four points.



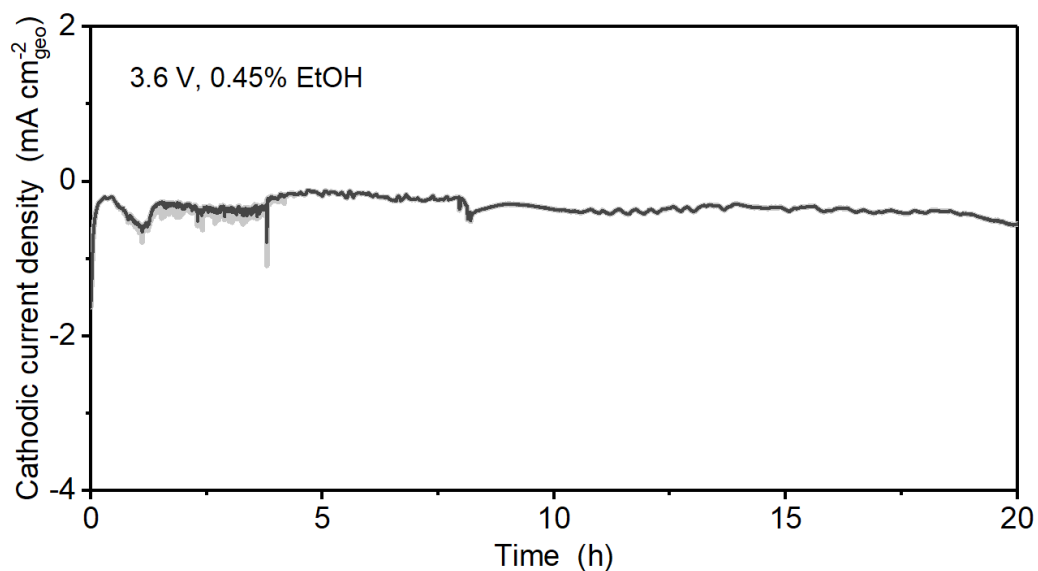
Supplementary Fig. S12. Current profiles at cell voltage of 3.6 V under varied EtOH concentration.



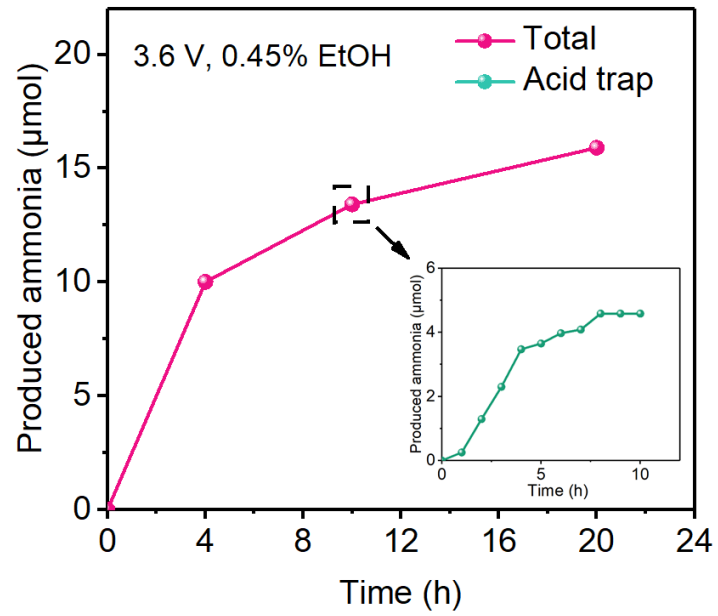
Supplementary Fig. S13. Distribution of detected ammonia in MEA and acid traps. No ammonia was detected in anodic acid trap, suggesting that little ammonia was taken out by feed gas at anode, which may be associated with acid environment induced by HOR reaction at anode.



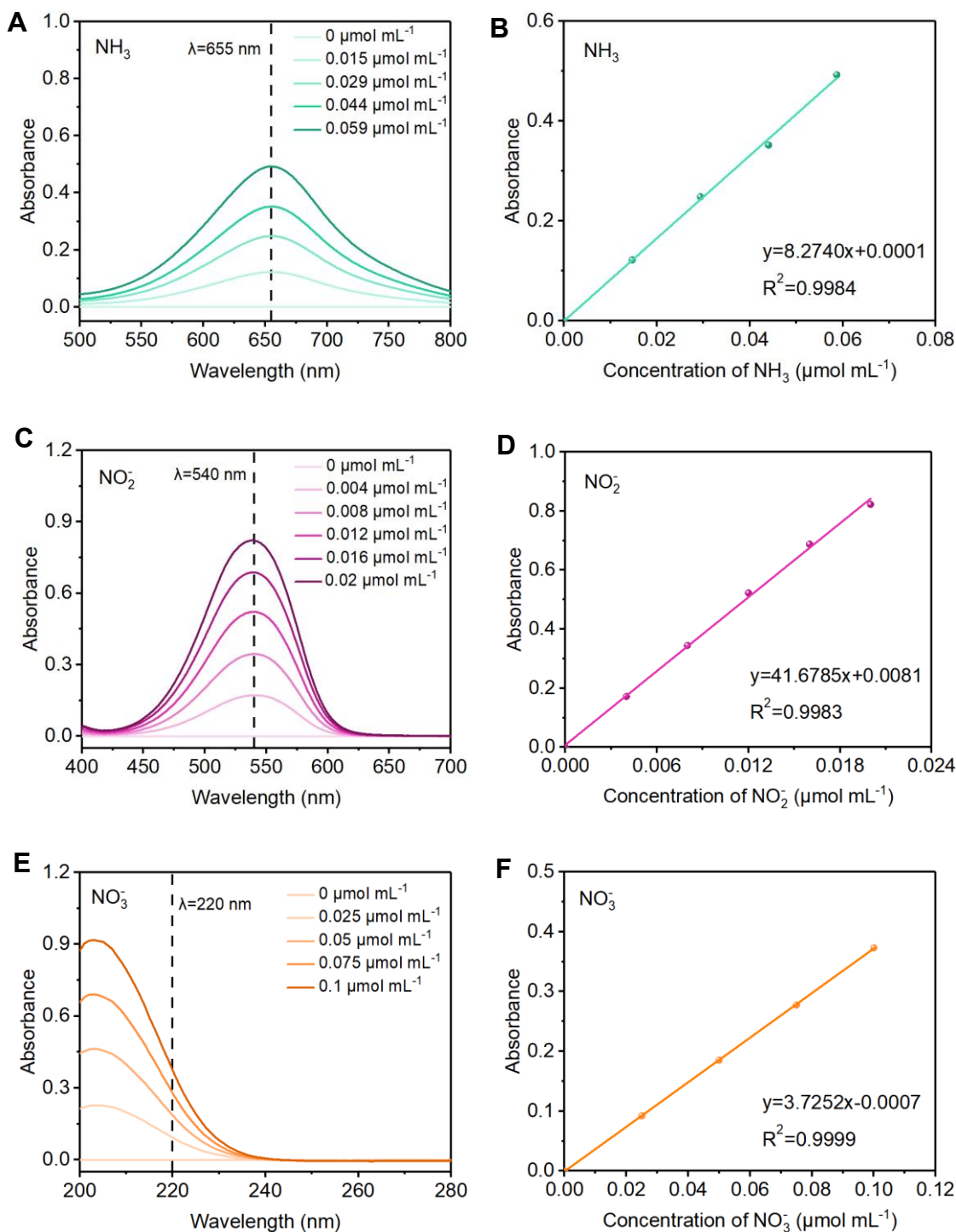
Supplementary Fig. S14. Quantification of produced ammonia by UV-Vis spectrophotometry coupled with indophenol blue method. To eliminate interfering effect of any soluble components in MEA, a suggested method of standard additions was employed.⁴ (A) UV-vis spectra of indophenol indicator-stained samples with addition of various extraneous ammonia. It should be noted that background correction was included by subtracting absorbance of blank solution. (B) Corresponding calibration curves made by linear regression fit of the samples' absorbance values at 655 nm.



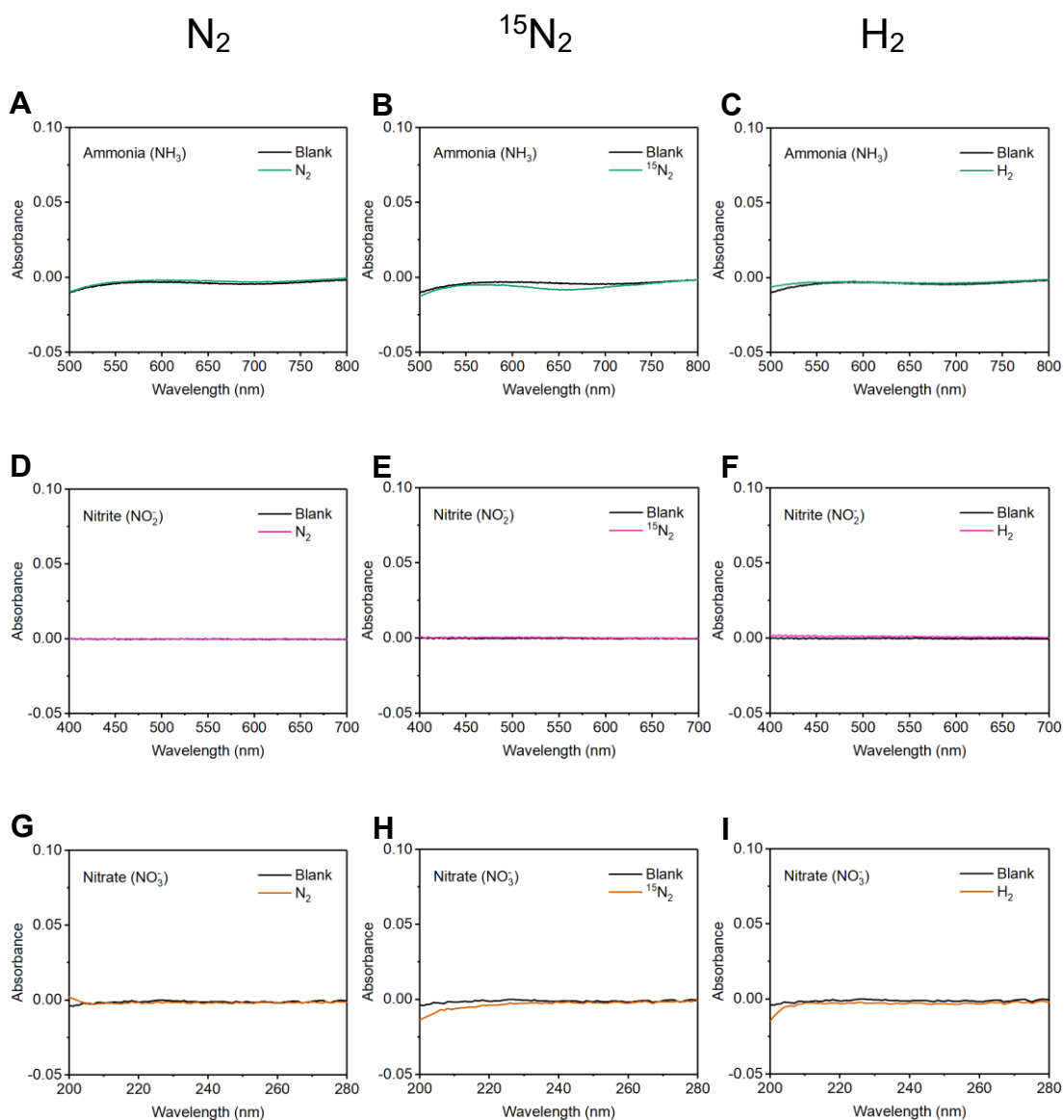
Supplementary Fig. S15. Longer-term chronoamperometric measurement at cell voltage of 3.6 V for 20 hours.



Supplementary Fig. S16. Ammonia production as a function of time. For the curve labelled as total, each point was obtained by independent electrochemical test. The inset shows the trend of detected ammonia in acid trap with time in 10 hours test.



Supplementary Fig. S17. Calibration curves obtained by UV-Vis spectrophotometry. (A) UV-Vis spectra of samples with given concentration of ammonia stained by indophenol blue method and (B) corresponding calibration curves made by linear regression fit of the samples' absorbance values at 655 nm. (C) UV-Vis spectra of samples with given concentration of nitrite stained by Griess method and (D) corresponding calibration curves made by linear regression fit of the samples' absorbance values at 540 nm. (E) UV-Vis spectra of samples with given concentration of nitrate and (D) corresponding calibration curves made by linear regression fit of the samples' absorbance values at 220 nm.



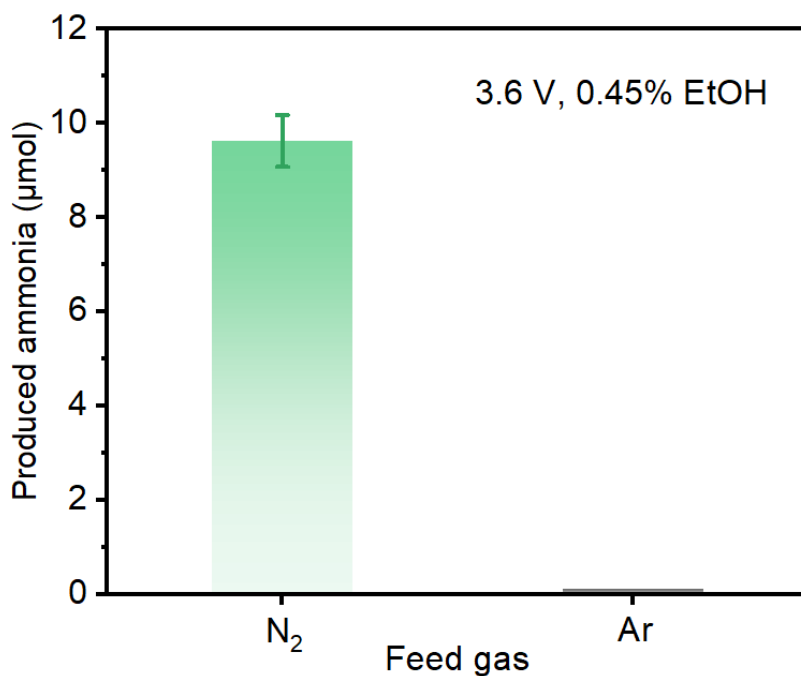
Supplementary Fig. S18. Detection of nitrogen-containing contaminations in feed gases. (A-C) Detection of possible ammonia in 0.05 M H_2SO_4 acid trap bubbled by (A) N_2 , (B) $^{15}\text{N}_2$ and (C) H_2 flow for 4 hours. (D-F) Detection of possible nitrite in 0.1 M KOH alkaline trap bubbled by (A) N_2 , (B) $^{15}\text{N}_2$ and (C) H_2 flow for 4 hours. (G-I) Detection of possible nitrate in 0.1 M KOH alkaline trap bubbled by (A) N_2 , (B) $^{15}\text{N}_2$ and (C) H_2 flow for 4 hours. Blank data refers to freshly prepared solutions. The flow rate here was the same as that during electrolysis (2 sccm).

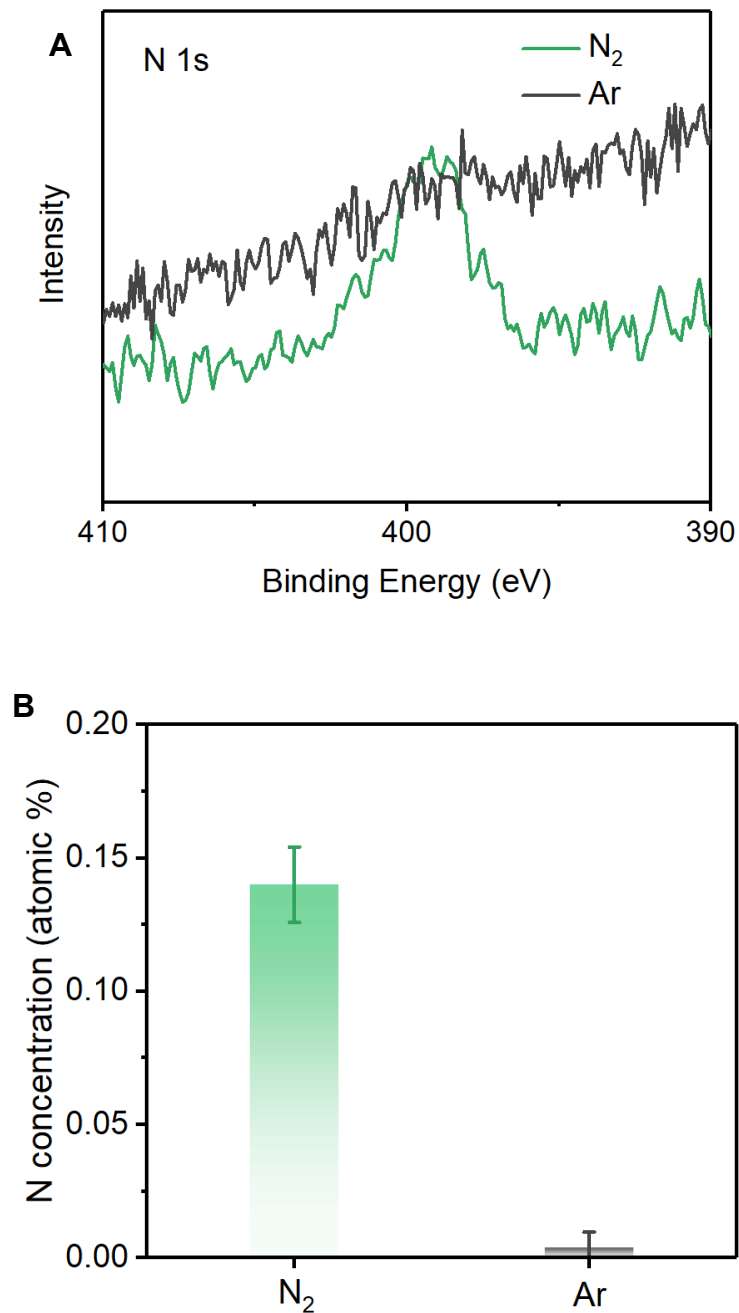
Table S1. Summary of gas purity analysis derived from Fig. S17-18

Gas	N ₂	¹⁵ N ₂	H ₂
Purity	99.999%	99%	99.999%
NH ₃ concentration (nmol mL ⁻¹)	0.4375	-0.9475	0.1765
NO ₂ ⁻ concentration (nmol mL ⁻¹)	-0.0121	0.0394	0.0850
NO ₃ ⁻ concentration (nmol mL ⁻¹)	-0.5637	-6.9258	-4.5367
NH ₃ amount (nmol)	5.2502	/	2.1175
NO ₂ ⁻ amount (nmol)	/	0.4723	1.0205
NO ₃ ⁻ amount (nmol)	/	/	/

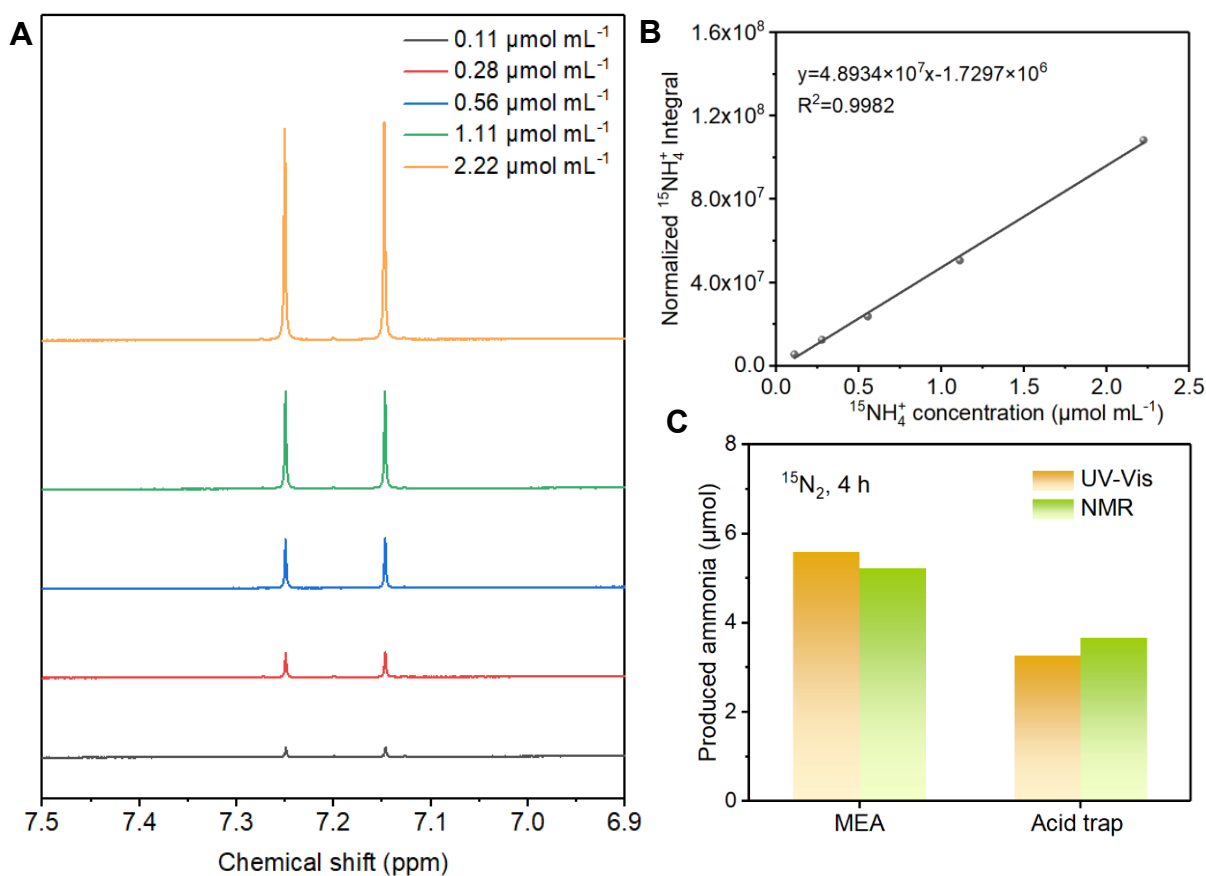
Note:

- 1) Negative concentration occurs when the absorbance of tested sample is lower than of blank sample.
- 2) Since negative value is meaningless when calculating impurities amount, “/” is employed when negative amount occurs.

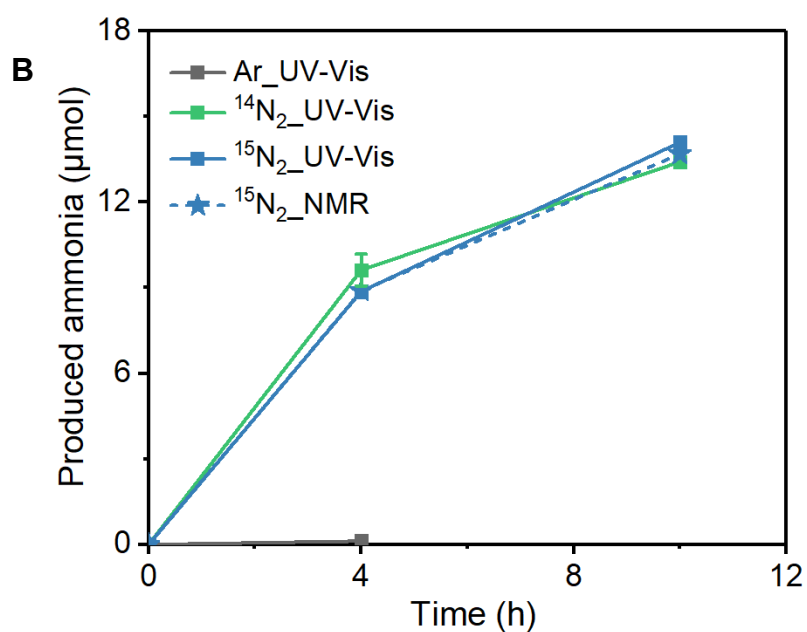
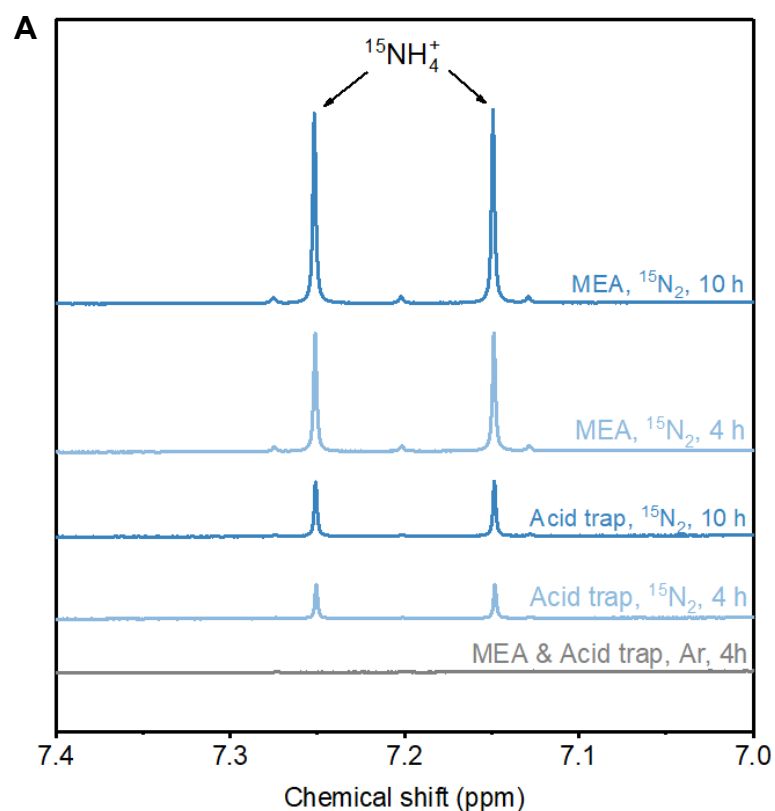
**Supplementary Fig. S19.** Comparison of produced ammonia with different feed gases.



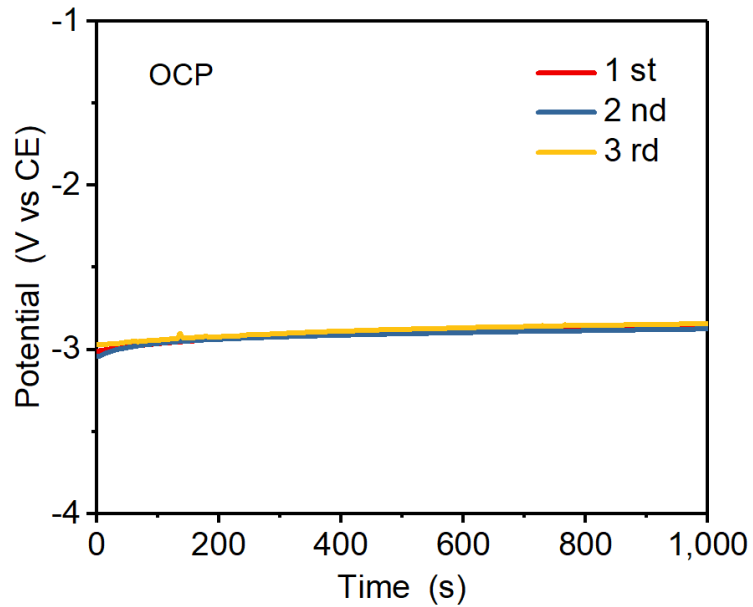
Supplementary Fig. S20. Comparison of XPS results obtained at feed of different gases. (A) Typical XPS spectra of N 1s for lithium deposits after electrolysis with feed gas of N₂ or Ar. (B) Nitrogen concentration on lithium deposits determined by corresponding XPS spectra. The error bars represent standard deviation for two locations (n=2). We would like to note that the nitrogen concentration obtained by XPS is a semi-quantitative result.



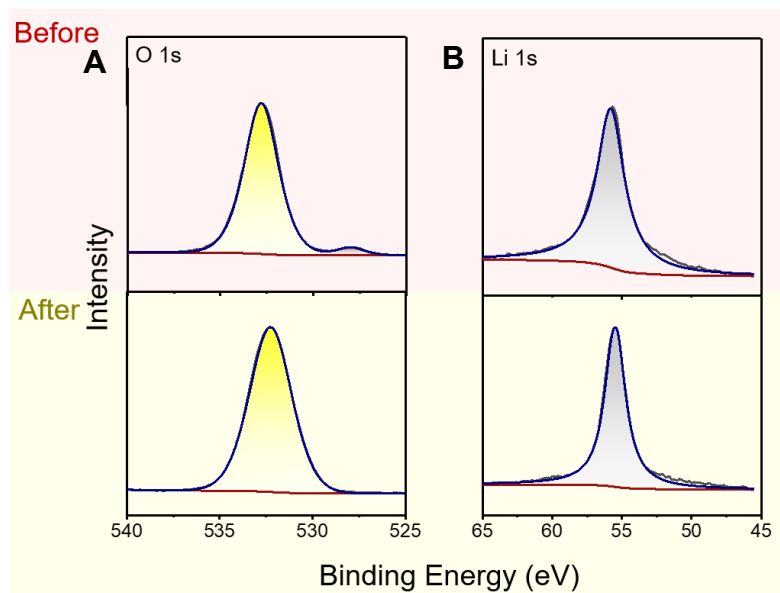
Supplementary Fig. S21. Quantification of $^{15}\text{NH}_4^+$ by nuclear magnetic resonance (NMR). (A) NMR spectra of samples with given concentration of $^{15}\text{NH}_4^+$. (B) Corresponding calibration curve made by plotting peak area versus $^{15}\text{NH}_4^+$ concentration. (C) Comparison of produced ammonia quantified by both UV-Vis spectrophotometry and NMR measurement. The ammonia was synthesis at cell voltage of 3.6 V for 4 hours with feed gas of $^{15}\text{N}_2$.



Supplementary Fig. S22. Control experiment confirming nitrogen reduction to ammonia. (A) NMR data of experiments with MEA or acid trap samples obtained after 4 or 10 hours of electrolysis fed with $^{15}\text{N}_2$ or Ar. (B) Evolution of amount of ammonia detected by UV-Vis spectrophotometry (solid lines and squares) and NMR (dash lines and stars) with Ar, $^{14}\text{N}_2$ or $^{15}\text{N}_2$ as feed gases.



Supplementary Fig. S23. Open circuit potential test after chrono-amperometric measurements presented in Fig. 4D. The results here were produced by three independent experiments.



Supplementary Fig. S24. Comparison of XPS patterns for lithium deposits collected before and after electrolysis. XPS spectra of (A) O 1s and (B) Li 1s at given scanning window. The samples were prepared, transferred and tested without exposure to air.

Table S2. Summary of electrochemical data with standard deviation related to Fig. 4E and 4F.

Experiment condition	Number of tests	Ammonia yield rate $\mu\text{mol h}^{-1} \text{cm}_{\text{geo}}^{-2}$	Total Faradaic efficiency %
3.3 V	2	2.06 ± 0.07	11.26 ± 1.23
3.6 V	2	2.41 ± 0.14	8.95 ± 1.72
3.9 V	3	2.41 ± 0.58	8.39 ± 3.49
4.2 V	2	1.92 ± 0.41	5.85 ± 1.07
Open circuit	2	0.51 ± 0.14	/

Note: The data was presented in the form of "Average \pm Standard deviation".

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1. X. Cai, F. Yang, L. An, C. Fu, L. Luo, S. Shen and J. Zhang, *ChemSusChem*, 2022, **15**, e202102234.
2. W. P. Utomo, H. Wu and Y. H. Ng, *Small*, 2022, **18**, e2200996.
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