Supplementary Information (SI) for Sustainable Energy & Fuels.

Plasma-coupled Electrochemical Ammonia Synthesis Using a Solid Acid Electrochemical Cell

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METHODS

Integrated reactor design and construction

The major components of the reactor shown in **Figure 1** and reproduced here as **Figure S1** are as follows:

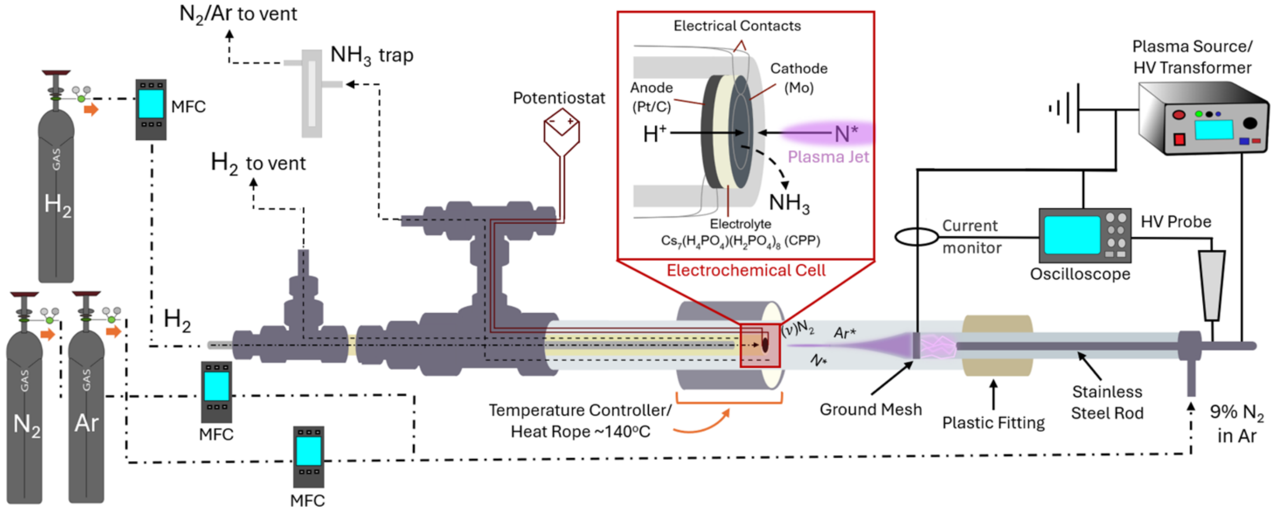

Figure S1*. A reproduction of* ***Figure 1*** *from the main text, included here to facilitate the discussion of the instrumental setup below.*

- A pulsed plasma power supply unit (Leap100, PlasmaLeap Technologies, Sydney, Australia) was used for generating the plasma jet. This source can deliver high voltage pulses up to 80 kV (peak-to-peak) with a repetitive pulse frequency ranging from 100 to 3000 Hz and a maximum output power of 400 W.
- A Tektronix 2 Series Mixed Signal Oscilloscope (MSO) to measure current-voltage waveforms within the plasma.
- A Tektronix P6025A high-voltage (HV) probe for measuring the applied plasma voltage.
- A Pearson TM current monitor model 4100 for measuring the current through the plasma.
- A Biologic SP200 potentiostat for applying/measuring current/voltage across the electrochemical cell

The electrochemical cell is mounted and sealed, anode-side-down, onto the end of an alumina tube (OD 0.5 in., ID 3/8 in.) using a silicone-based high temperature sealant (Ultra Red RTV from Permatex). Four insulated wires serve as the sense and power cables for the anode and cathode, connecting the cell to the potentiostat outside the reactor using a pseudo-four-point probe configuration where the voltage and current leads are connected at the cell electrodes to create two contact points at the cell. The cathode side of the cell faces a plasma jet formed within a borosilicate Pastuer pipette. A high voltage rod is located centrally within the pipette, ending 3 inches before the tip and positioned 1 cm upstream from a grounded stainless steel mesh (1 cm wide) wrapped around the outside circumference of the pipette. The plasma flows through the pipette and exits through a 0.80 mm^2 opening into a larger (1 in. OD) quartz tube that encloses the plasma jet reactor and the electrochemical cell with its alumina support. The plasma jet takes the shape of an elongated cone about 1 mm in diameter and approximately ¾ of an inch in length. The distance from the tip of the glass pipette to the cathode of the electrochemical cell is 1 inch.

Prior to experimentation, the temperature within the reactor is calibrated by replacing the electrochemical cell with a thermocouple, such that the thermocouple is located in the same location that the cell would be during operation. The reactor is then heated using heat rope wrapped around the exterior of the quartz tube, and the current through the heat rope is adjusted using a variable AC transformer (Payne Engineering 18TBP-1-15) until the temperature within the reactor stabilizes at 140 °C.

During operation, the thermocouple is replaced with the electrochemical cell and the reactor is maintained at 140 °C using the same power settings to power the heat rope. H_2 gas is supplied to the anode side of the cell via stainless steel tubing at a flow rate of 100 sccm. At the cathode side, the gas supplied to the plasma generator via the glass pipette is 9% N_2, balance Ar, at a flow rate of 275 sccm. The exhaust gas from the cathode is directed to a glass fritted bubbler where any ammonia produced is dissolved in 25 mL of deionized water and subsequently monitored for ammonia synthesis using the salicylate method. The end of the plasma jet plume was observed to be 0.25 inches from the cathode in all experiments. The distance from the cell to the glass pipette was chosen to prevent arcing of the plasma jet to the potentiostat.

Cell materials

The electrolyte $Cs_7(H_4PO_4)(H_2PO_4)_8$ (CPP) forms upon reaction between CsH_2PO_4 (CDP) and $CsH_5(PO_4)_2$ and is stable at temperatures between 90 °C and 150 °C. The precursors, CDP and $CsH_5(PO_4)_2$, were prepared via precipitation from aqueous solutions as reported elsewhere.[1, 2] CPP is then formed as the electrolyte layer *in-situ* when a well-mixed mixture of CDP and $CsH_5(PO_4)_2$ in a 5:2 molar ratio is heated above 90 °C.[1] Other components of the cell are obtained commercially: naphthalene (Alfa Aesar, Lot #10193966); carbon black (Alfa Aesar, Lot #Q29C020); HiSPEC-3000, 20 w% Pt on carbon (Alfa Aesar Lot #13E066).

Anode supported half-cell fabrication

The anode-supported half-cell is prepared by pressing the following layers in sequence onto a stainless steel mesh for support: a carbon black microporous layer to aid in gas diffusion, a Pt/C + CPP composite anode, and a 210 µm thick CPP electrolyte layer. The stainless steel mesh (Serra Laser & Waterjet) is shaped into a disc, 14.85 mm in diameter. The microporous layer is formed from a mixture of CDP, naphthalene, and carbon black (mass ratio 3:2:1), with a total mass of 46 mg. The mixture is sieved through a 53 micron mesh and then layered onto the stainless steel support using a razor blade chopping method to ensure uniform distribution across the mesh. The anode, comprised of a mixture of CDP, $CsH_5(PO_4)_2$, and Pt on carbon black in a 3.8:2.2:1 mass ratio (total of 18 mg), is layered directly onto the microporous layer using the same chopping method and pressed at a pressure of 100 MPa for 3 seconds. Atop the microporous layer, 120 mg of a 3.8:2.2 mass ratio of CDP and $CsH_5(PO_4)_2$ is pressed at 140 MPa for 1.5 min to form the electrolyte layer. In both the anode and the electrolyte layers, the mixture of CDP and $CsH_5(PO_4)_2$ are anticipated to form CPP *in situ*. The stainless steel mesh, microporous layer, anode, and electrolyte layer are wrapped in ¼" PTFE tape and pressed again at 28 MPa for 1 second, leaving an exposed area of electrolyte (0.57 cm^2).

Cathode layer deposition and characterization

A Mo thin film was sputtered directly onto the anode supported half-cell via Radio Frequency sputtering in an AJA Orion Sputter System. The film was sputtered for 5 minutes at 150 W in a pure Argon atmosphere (2 mTorr total pressure). Simultaneously, deposition was performed on a 1 × 1 cm (100) oriented silicon substrate, and the resulting film was characterized via X-ray reflectivity (XRR) and grazing-incidence X-ray diffraction (GIXRD). The half-cell is insufficiently flat for such characterization. X-ray measurements were made with a Rigaku Smartlab X-ray diffractometer using a Cu Kα X-ray source. For XRR, a step size of 0.015 degrees in 2θ and a scan speed of 0.5 degrees/min were used from 0-6 degrees in 2θ. For GIXRD, an omega offset of 0.5 degrees, a step size of 0.2 degrees in 2θ, and a scan speed of 2 degrees/min were used.

XRR patterns are modeled and fit using Motofit,[3] a neutron and X-ray reflectometry refinement package for Igor Pro (WaveMetrics, Inc., Lake Oswego, OR, USA) that uses the Abeles matrix and Parratt recursion methods to perform least squares fitting of reflectometry patterns. The refined X-ray scattering length density (SLD) of the Mo films in Figure S2a and S2b are 70×10^{-6} Å^{-2} and 69×10^{-6} Å^{-2}, respectively, leaving each film with a density of ~ 91% of the theoretical density of pure metallic Mo (I m -3 m) with an X-ray SLD of 76×10^{-6} Å^{-2}.

Cell characterization

Scanning electron microscopy (SEM) images of the complete electrochemical cell were collected using a JEOL JSM-7900FLV and a 5.0 kV electron beam. A cross section of the film was achieved by cutting an unused cell in half with a razor blade and mounting a fractured piece of the cell vertically onto an SEM stub.

Electrochemical characterization

Impedance spectra were collected at 140 °C with 50 sccm H_2 flowing to both electrodes, for which the cells were placed into a conventional electrochemical cell holder, in turn placed in a high temperature oven. For these measurements, 19 mm diameter cells were utilized. The preparation of the anode side of the cell was identical to the electrochemical cells used in the PCE reactor, except that amount of material was scaled up to account for the larger diameter (using 75 mg of microporous layer mixture and 30 mg of anode mixture to achieve similar layer thickness in the larger cells). Freestanding 0.4 mm thick, 19 mm diameter pellets of the CPP mixture (a 3.8:2.2 mass ratio of CsH_2PO_4 to $CsH_5(PO_4)_2$) pressed at 210 MPa for 5 minutes were used as the electrolyte layer. A cell with a Pt/C cathode was prepared by sandwiching two identical Pt/C anodes onto both sides of a CPP pellet and wrapped around the edges with ¼" PTFE tape. For the Mo and Mo + Pt/C cells, the Mo layer was sputtered using the same sputtering procedure described above. XRR of the Mo films deposited for the 19 mm diameter cells indicate a Mo film thickness of 15.2 ± 0.3 nm (**Figure S2**) For the Mo cathode film, the Pt/C anode and CPP electrolyte with the Mo film opposite the anode were wrapped in ¼" PTFE tape, leaving an exposed Mo area of 1.49 ± 0.04 cm^2. Carbon paper with a microporous layer (Fuel Cell Store) was placed directly over the Mo film, followed by a stainless steel mesh and the whole cell was wrapped in ¼" PTFE tape once more. The Mo + Pt/C cell was prepared in an identical manner to the Pt/C cell, except that the CPP pellet sandwiched between the two Pt/C electrodes has the 15.2 nm Mo film deposited on the cathode side of the CPP pellet. The Pt/C and Mo + Pt/C cells both have a geometric surface area of 2.8 cm^2.

Electrochemical impedance spectra were measured with a Biologic SP300 potentiostat in pseudo-four probe geometry. All impedance spectra were measured at open circuit potential with a perturbation amplitude of 100 mV. The frequency ranges for the Pt/C and Mo/Pt/C cells were 5 MHz – 10 mHz, whereas for the Mo cell the frequency range was extended to 5 MHz – 2.5 mHz to capture the low frequency impedance arc. For ease of comparison between the electrode responses, impedance data is only shown up to 230 kHz, thereby removing high frequency, non-electrode contributions from all EIS data in this work.

Current collectors

Two three-inch strands of silver wire are molded to form a ¼ inch diameter circle with two equal lengths of wire protruding from the side of the circle. Each strand of wire is then mounted to the anode and cathode side of the electrochemical cell using 4 spot applications of silver paste each. After application of silver paste to the Mo cathode, the exposed surface area of the cathode is $0.30 \pm 0.01\ \text{cm}^2$. As a result, the surface area that is used in current density and ammonia synthesis rate calculations is $0.30 \pm 0.01\ \text{cm}^2$.

Plasma characterization

Charge-voltage Lissajous figures were generated to analyze discharge capacitance. The plasma power dissipation was calculated using the following equation:

$$P_{dissipated} = f \int_0^t V(t) \left[I_{measured} - C \frac{dV}{dt} \right] dt$$

where *f* is the frequency, *V* and *I* are the voltages and current measured by the oscilloscope, and C dv/dt is the displacement current.

The current-voltage characterizations of the N_2/Ar plasma are provided in **Figure S6.** The plasma power source used in this experiment generates a series of plasma pulses alternating in polarity (**Figure S6a)**. With power supply input parameters of 175 V, 500 Hz, and 83 μsec pulse width, the plasma voltage peaks at ± 18.5 kV and ± 0.26 A. Integrating the plasma voltage and charge over the time period of one pulse provides an estimate for the average dissipated (absorbed) power consumption of 7.3 W (**Figure S6b**).

Quantification of ammonia production

Ammonia generated in the cathode/plasma side of the electrochemical cell was trapped in 25 mL of deionized water in a glass fritted bubbler. After each 5 minute chronoamperometry experiment (**Figure 4, Figure S5**), the bubbler solution was collected into a scintillation vial and replaced with a clean glass fritted bubbler filled with 25 mL of fresh deionized water. As a result, each measurement of the ammonia synthesis rate is a time-averaged measurement over the course of the entire 5 minute experiment.

Ammonia production was quantified using the salicylate method, described in detail by Le and Boyd.[4] Briefly, a sodium salicylate solution containing 2.7 M sodium salicylate (Sigma Aldrich, Lot #K55199701417) and 0.98 mM sodium nitroprusside (Sigma Aldrich, Lot #BCCM9015) is prepared and sealed tightly to minimize contamination from trace ammonia in the atmosphere. An alkaline sodium hypochlorite solution is prepared just prior to operation to minimize degradation of the solution. The alkaline hypochlorite solution contains 0.075 M sodium hypochlorite (Sigma Aldrich, Lot #MKCW5770), 0.35 M sodium citrate tribasic (Sigma Aldrich, Lot #SLCC2517), and 0.41 M sodium hydroxide (Fisher Chemical, Lot #180136). A 5 mL aliquot of the bubbler solution from the ammonia trap is analyzed by adding to it 1 mL of the alkaline sodium hypochlorite solution and 0.6 mL of the sodium salicylate solution. The resulting solution is stirred and stored in a dark box for 1 hour.

UV-Vis absorption measurements are taken of the 1 hour aged solution using a UV-Vis-NIR spectrophotometer (Agilent Cary Series) and the absorption intensity at 651 nm is recorded. A four-point calibration curve is created by adding known quantities of ammonium chloride (Sigma Aldrich, Lot #SLCK6884) to a series of solutions of deionized water, producing standard concentrations of 0.36 mg/L, 0.61 mg/L, 0.97 mg/L, and 1.22 mg/L NH_3. The standard solutions are prepared in an identical manner to the sample solutions and their absorption at 651 nm is measured. To calculate the ammonia content in the unknown sample solutions, the sample solutions are compared to the standard solution with the nearest absorption ratio using

$$C_u = C_s \times \frac{A_u}{A_s}$$

Where C_u is the concentration of the unknown solution, C_s is the concentration of the standard solution, A_u is the absorption of the unknown solution, and A_s is the concentration of the standard solution.

All calculations for NH_3 synthesis include two background subtractions. The first is a subtraction in the UV-Vis signal to account for the absorbance of a blank indophenol blue solution prepared with fresh DI water. The second background subtraction is in the observed NH_3 synthesis rate which comes from measuring the NH_3 collected from N_2/Ar gas flow through the reactor without the addition of an electrochemical bias or plasma (0.05 nmol $NH_3/s \cdot cm^2$).

Energy consumption and efficiency calculations

The total power consumption is calculated as the sum of the dissipated plasma power (7.3 W) and the power consumed from the electrochemical cell, calculated as the product of the average current passing through the cell for the duration of the experiment and the bias across the cell (-2 V). The energy consumption (kWh/mol) is calculated by: Power consumed (W) / [NH_3 synthesis rate (mol/s) × 3600000]. The average energy consumption in the PCE condition is 6 ± 2 MWh/mol. The energy consumed in sustaining the plasma is responsible for 99.85% of the energy consumed in this PCE process.

The energy efficiency (output energy of NH_3 produced/input energy from the plasma and electrochemical cell) is calculated using a lower heating value of ammonia of 18.6 MJ/kg or 316.2 kJ/mol NH_3 as follows: (316.2 kJ/mol NH_3 / [6000 kWh/mol NH_3 × 3600 kJ/kWh]) × 100% = 0.0016% ± 0.0006%.

Impact of nitrogen plasma on Mo cathode film

A 64 nm Mo film on a 1x1 cm (1 0 0) silicon substrate was exposed directly to a nitrogen/argon plasma jet for 10 minutes. The tip of the plasma jet was located 1 inch away from the Mo film, contained 500 sccm Ar and 100 sccm N_2 (17% N_2 balance Ar), and was powered at a frequency of 100 Hz, input voltage of 250 V, and a duty cycle of 63 μsec. Chemical composition analysis via X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific ESCALAB 250Xi with a 500 μm diameter monochromatic Al Kα X-ray source. A flood gun was used to prevent charge accumulation on the surface, and the instrument's base pressure was below 10^{-7} mbar at the time of XPS measurement. XPS spectra were measured in the N 1s and

Mo 3p region from 435-375 eV to qualitatively compare the surface composition of the molybdenum film before and after exposure to the nitrogen plasma.

RESULTS

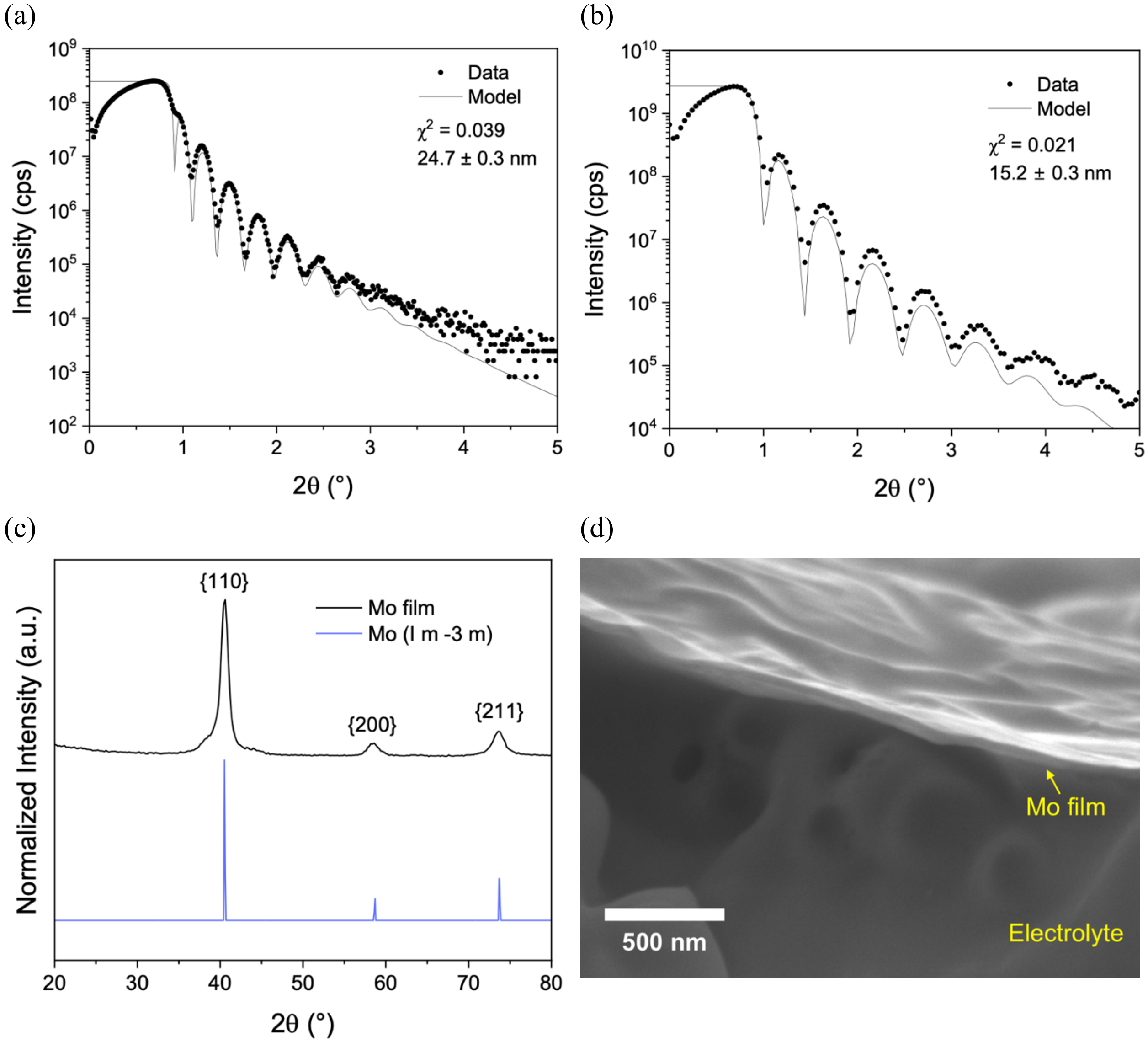

Figure S2. Characterization of sputtered deposited Mo films: **(a)** XRR measurement of an Mo film, 24.7 ± 0.3 nm in thickness, deposited on Si (100) alongside the film used in in the ammonia synthesis experiments; **(b)** XRR of an Mo film, 15.2 ± 0.3 nm in thickness, deposited on Si (100) alongside the film used in EIS measurements; **(c)** GIXRD pattern (omega offset = 0.5 °) of a representative Mo film (24.7 ± 0.3 nm) revealing a diffraction pattern consistent with metallic Mo; and **(d)** SEM cross-section of a representative electrochemical cell highlighting the structure of the dense Mo thin films serving as the cathode. X-ray measurements in (a)-(c) were made using Cu Kα radiation.

Figure S3. A photograph of the 64 nm Mo film on a 1x1 cm (1 0 0) silicon substrate being exposed directly to a nitrogen/argon plasma jet for 10 minutes.

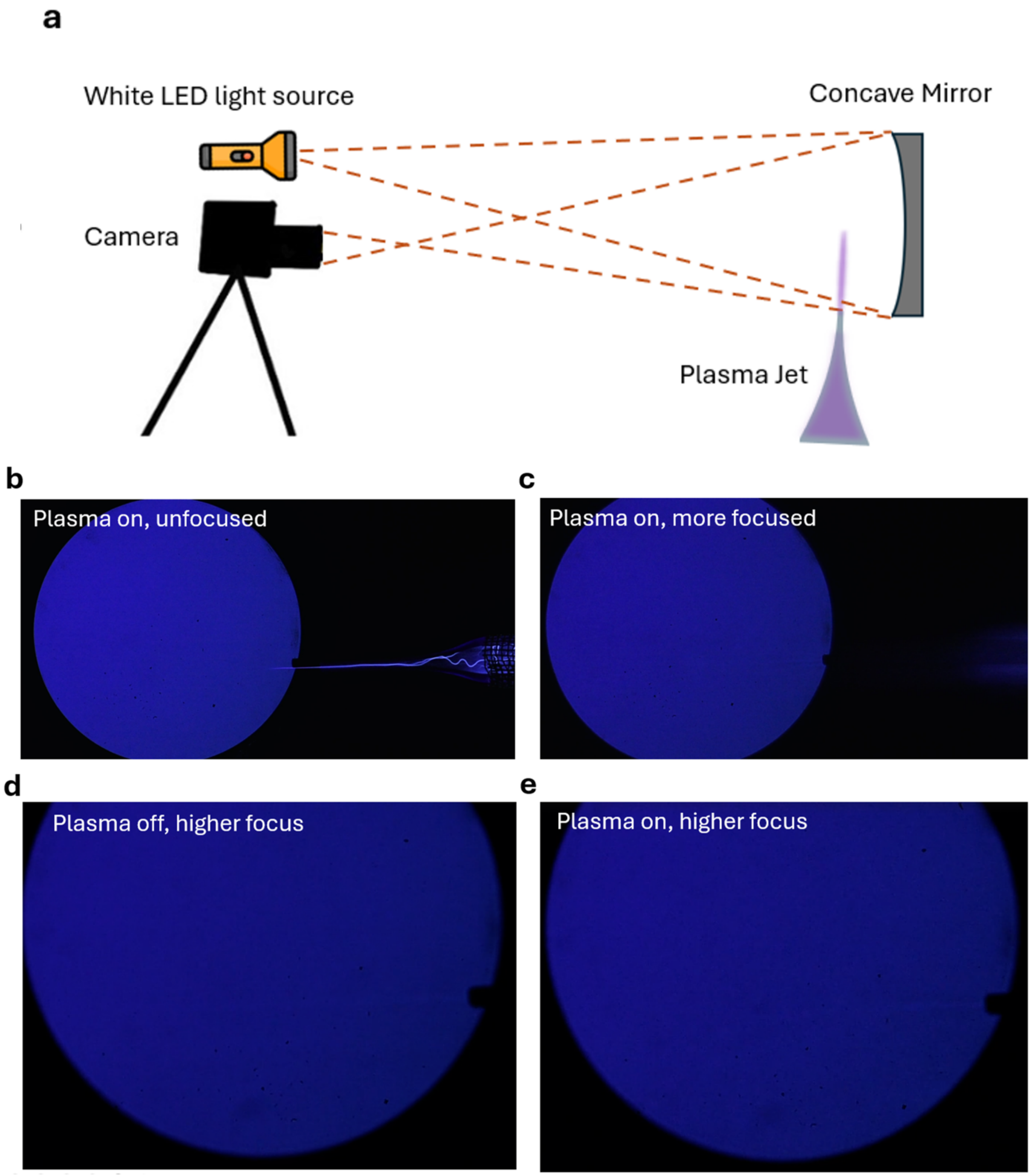

Figure S4. (**a**) Schematic of the Schlieren optics set-up. (**b-e**) images of Schlieren optics for plasma jet. The lack of contrast between (**d**) plasma off and (**e**) plasma on images indicates that there is no gradient in their respective refractive index with the surrounding air. This means that both of these systems operate at similar temperatures and that there is no temperature increase in the actual plasma jet or after the plume, hence an atmospheric cold plasma.

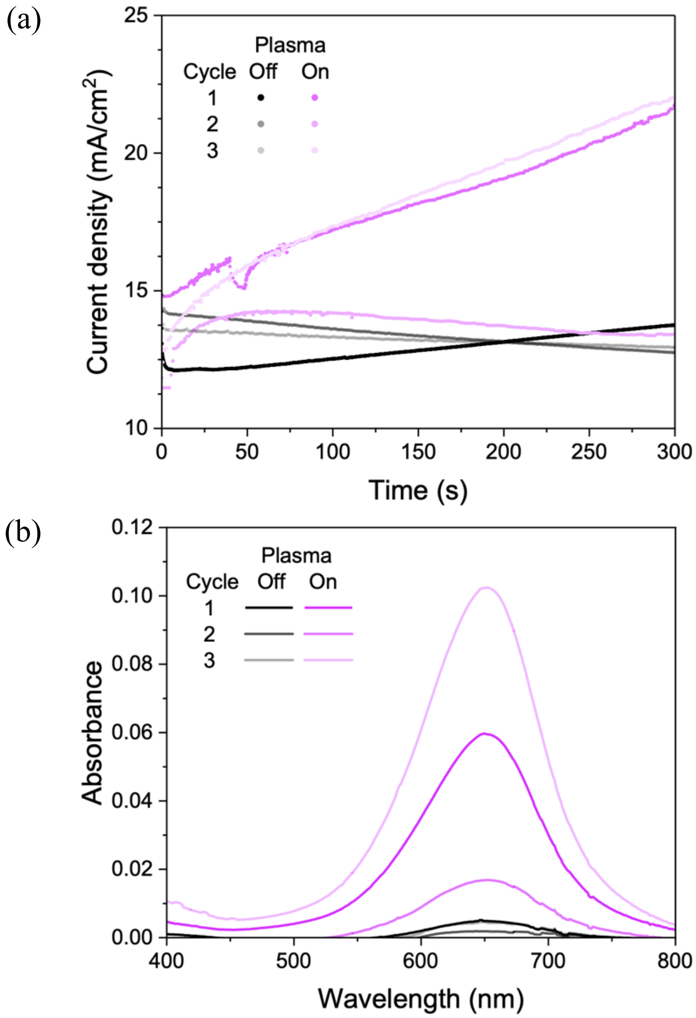

Figure S5. (a) Chronoamperograms comparing the current response subject to a -2 V electrochemical bias with the plasma off (electrochemistry only, black) and plasma on (PCE, purple) for all six experiments. All 6 experiments were conducted on the same electrochemical cell within 5 - 7 minutes of each other in chronological order. Cycle numbers (1-3) indicate the chronological order each experiment was measured, beginning with the plasma off condition. The data from cycle 3 are replotted in **Figure 4a** as representative datasets for each condition. The short dip at t = 50 s in cycle 1 (plasma on) is due to the plasma accidentally turning off for 10 seconds before being turned back on. **(b)** Raw UV-Vis data depicting the relative quantities of ammonia synthesized from each trial collected using the salicylate method. Due to instability in the glow-discharge regime of the plasma jet, the plasma produced a significantly reduced current response in the cell in the PCE condition of Cycle 2. These sudden changes between glow discharge and filamentary discharge regimes occurred periodically and the latter coincided with smaller plasma plumes and less pronounced current responses in the cell. As a result, we excluded the ammonia synthesis performance of this individual trial from the average ammonia synthesis rate in the PCE condition reported in the manuscript.

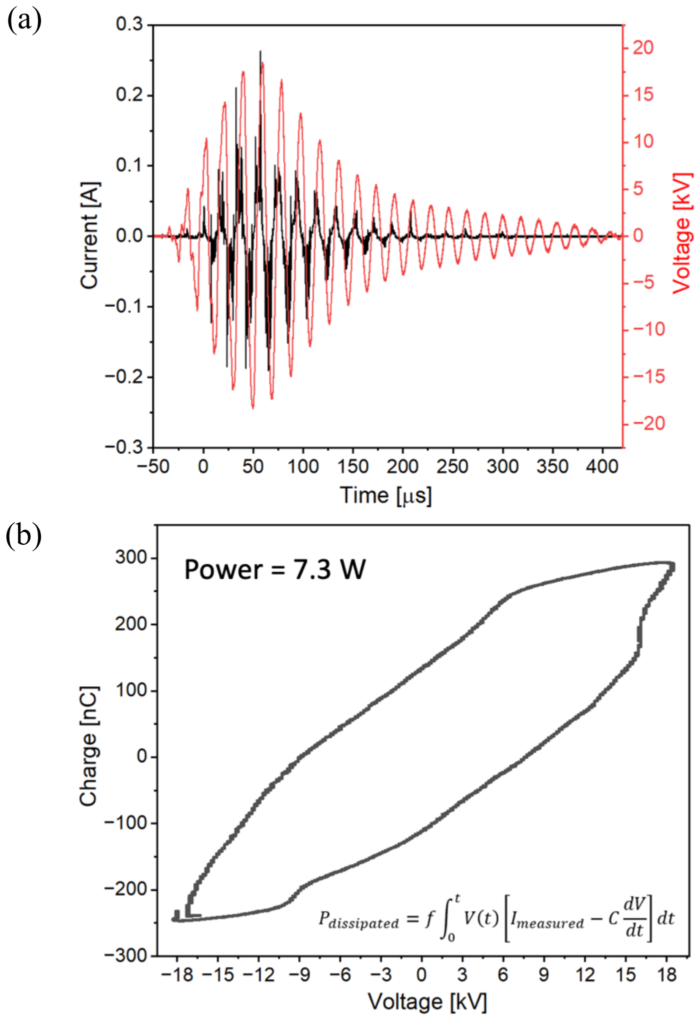

Figure S6. (a) The voltage and corresponding current behavior in a single plasma pulse, indicating peak voltages of ± 18.5 kV and peak currents of ± 0.26 A. **(b).** A Lissajous plot for the plasma jet used in the plasma-electrochemical experiments. The average power utilization of the plasma is 7.3 W.

REFERENCES

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