



Synergistic plasma-assisted electrochemical reduction of nitrogen to ammonia

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Experimental Methods

Plasma Operation

A custom-built plasma jet reactor was fabricated consisting of a 3.2-mm-diameter stainless steel rod electrode in the center of a 10-mm-inner-diameter (13 mm outer diameter) glass tube fitted inside a 13-mm-inner-diameter (16 mm outer diameter) copper tube electrode (Fig. 1a). The inner glass tube extended ~ 5 mm beyond the end of the copper tube electrode. High purity N₂ (99.99%, Welder Supply) and He (99.99% Welder Supply) were mixed at a 1:1 volumetric ratio and flowed through the glass tube at a total rate of 2.5 std L min⁻¹. The plasma was driven by an AC power supply (PVM500) using a sinusoidal waveform at ~20 kHz. All reported plasma measurements were performed at an applied power of 8.4 W. The power supply ground was also connected to the copper tube, which along with the high gas flow rate prevented plasma arcing to the electrolyzer electrode. Under these conditions, the visible plasma glow discharge was observed to extend ~ 1 cm beyond the end of the glass tube exit (Fig. 1c). The plasma jet reactor was inserted through a machine-milled hole fit to the diameter of the glass tube in the end plate of the electrolyzer cathode side, with the copper electrode just outside the electrolyzer end plate. The plasma reactor tube was secured and sealed gas-tight with epoxy. The distance from the tip of the stainless steel rod electrode to the surface of the electrolyzer membrane electrode assembly was 1.7 cm.

Electrochemical Measurements

Commercially available PEM reversible fuel cells (Horizon, FCSU-023) were used in electrolyzer mode in this work. The electrolyzer consisted of two stainless steel grids (one for the anode and one for the cathode), two carbon Toray paper sheets as gas diffusion layers, and one membrane electrode assembly (MEA) with catalyst particles on either side of a sulfonated polytetrafluoroethylene (i.e., Nafion) proton-exchange membrane. The particulate catalyst material was the same for both electrodes (Pt/C), and was dispersed on the MEA following

standard hot press methods. The projected active area of the MEA was 5 cm². Deionized liquid water (18 MΩ-cm) was circulated through the anode chamber at 35 mL min⁻¹ for the duration of all experiments and for > 1 h prior to measurements. The N₂/He gas was flowed through the plasma reactor through the cathode chamber for > 1 h prior to measurements, though the actual plasma was ignited only ~ 1 min before measurements under plasma conditions. An SP-200 model Bio-Logic potentiostat was used to apply DC bias to the electrolyzer MEA and to measure current, through pins in contact with the current collector metal grids at either electrode. The *J-V* behavior was measured by sweeping the voltage at a scan rate of 5 mV s⁻¹. The current density was determined using the full projected area of the active part of the MEA (5 cm²). During NH₃ production measurements, the applied bias to the electrolyzer was held constant for 1 h while the cathode gas output was bubbled through a 50 mL reservoir of deionized water. To improve reproducibility, the electrolyzer was left under idle conditions for > 3 h between ammonia production measurements.

Ammonia Detection

A common colorimetric method for the detection and quantification of ammonia was employed by mixing 16 drops (8 drops from each bottle of the indicator kit) of an ammonia indicator dye (API Ammonia Test Kit) in a sample of 10 mL from the cathode output reservoir solution after each 1 h measurement. The electrolyzer cathode gas output was bubbled through this solution during the experiment, and the presence of dissolved ammonia changed the indicator dye color. A second reservoir in series with the gas output from the first reservoir confirmed that effectively all the ammonia was captured in the first reservoir. To quantify ammonia production, the absorbance of a sample of the reservoir indicator dye solution was measured with a UV/vis spectrometer (PerkinElmer Lambda 950) within 10 min of the completion of the 1 h potentiostatic measurement. An external calibration was produced using variable concentrations of NH₄Cl to correlate the absorbance peak intensity to the mg L⁻¹ of dissolved ammonia. The ammonia production rate at each condition was determined by the average of at least three separate measurements. Additional indicator dyes were also

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used in separate measurements to test for the presence of nitrates (API Nitrate Test Kit), nitrites (API Nitrite Test Kit), and hydrazine (Hach 184900 Model HY-2). For electrolyzer bias in the absence of plasma, none of these byproducts were detected. With the plasma on, appreciable amounts of nitrate (but less than the ammonia) and small amounts of nitrite and hydrazine were detected.

Optical Emission Spectroscopy

Optical emission spectroscopy (OES) was performed on the N_2/He plasma by detaching the plasma jet electrode from the PEM electrolyzer and positioning the optical probe perpendicular against the inner glass tube of the plasma jet electrode at the tip of the device near the plasma discharge. An optical fiber connected to an Ocean Optics S2000 spectrometer recorded the emission data. Figure S1 shows characteristic spectra for the plasma at operating conditions. The spectra is similar to that reported for a DC N_2 plasma jet discharge, with peaks in the 300 – 400 nm range attributed to the second positive system of the nitrogen molecule ($N_2(C^3\Pi_u-B^3\Pi_g)$), and peaks in the 380 – 440 nm range attributed to the first negative system of the nitrogen molecular ion ($N_2^+(B^2\Sigma_u-X^2\Sigma_g)$).¹ However, unlike the reported DC plasma, notable peaks of the first positive system of the nitrogen molecule ($N_2(B^3\Pi_g-A^3\Pi_u)$) in the 500 – 800 nm range were not observed, nor were NO emissions observed in the 250 – 300 nm range, since the AC plasma emission herein was measured in the glass tube before exposure to air.¹ He emission peaks in the 580 – 710 nm range were not clearly observed either, likely because the intensity of these emissions is much less than the nitrogen emission peaks.²

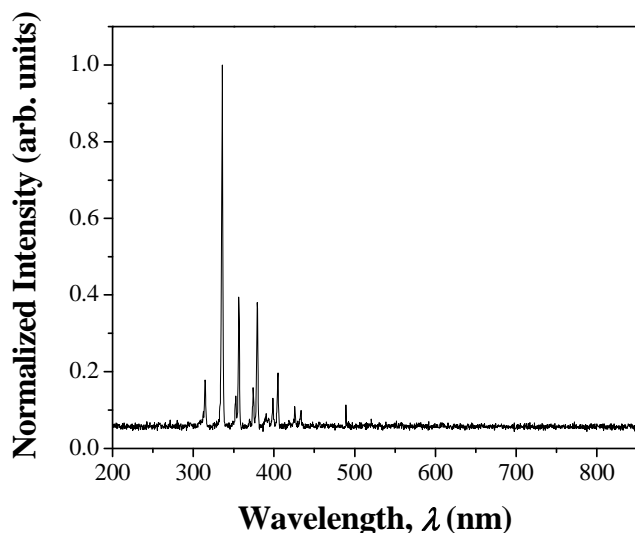


Figure S1. Optical emission spectra of the AC plasma discharge for N_2/He flow.

Electrolyzer Open-circuit Potential

The open-circuit potential, E_{oc} , of the PEM electrolyzer was monitored as a function of time for different operating conditions as shown in Figure S2. Prior to starting measurements, the electrolyzer was allowed to reach steady-

state conditions with water flowing to the anode and gas flow to the cathode in the absence of plasma. At this condition, the steady-state E_{oc} was ~ 0 V (Fig. S2, zone 1). Upon plasma ignition at the cathode, the PEM electrolyzer E_{oc} began to steadily rise before slowing its increase, and reached 0.37 V after 1 h of active plasma impinging on the electrolyzer cathode (Fig. S2, zone 2). All ammonia detection measurements over the course of this study were performed for 1 h, making the E_{oc} during this period the most relevant to the experimental conditions. Upon turning off the plasma, the E_{oc} decreased rapidly at first before slowly declining (Fig. S2, zone 3). Turning the plasma back on led to a rapid rise in E_{oc} followed by a slow increase to as high as 0.45 V after another hour of active plasma at the cathode (Fig. S2, zone 4). The dips in E_{oc} during this period corresponded to brief interruptions in the anode water circulation. Turning the plasma off again led to an initial rapid drop in E_{oc} followed by a slow decline (Fig. S2, zone 5). Stopping the gas flow to the cathode caused a further drop in E_{oc} (Fig. S2, zone 6).

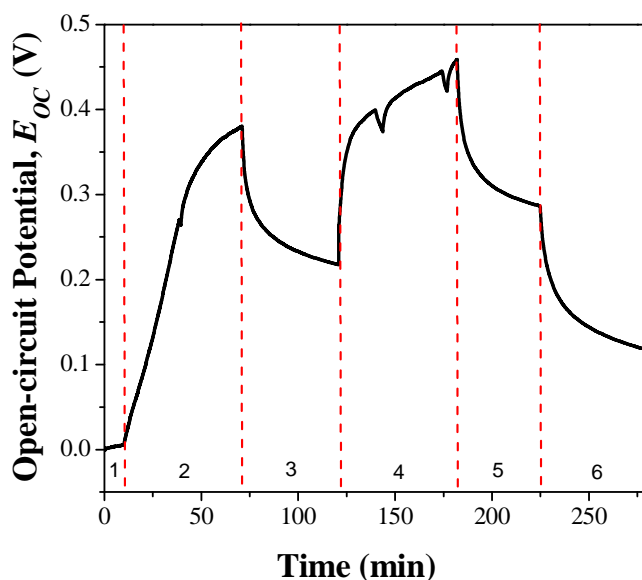


Figure S2. Open-circuit potential for the PEM electrolyzer vs. time for various operating conditions: (1) gas flow to cathode, no plasma, (2) gas flow to cathode, plasma on, (3) gas flow to cathode, no plasma, (4) gas flow to cathode, plasma on, (5) gas flow to cathode, no plasma, (6) no gas flow to cathode, no plasma. Liquid water was circulated at the anode for all conditions.

Current Density vs. Time Performance

For electrolysis conditions of simultaneous applied bias with plasma (BWP), the PEM electrolyzer current density was observed to decrease sharply over the first ~ 5 min of plasma operation and then settle to a fairly stable value as shown in Figure S3. This initial decline in current density at a constant applied bias was attributed to additional dehydration of the membrane surface from plasma dissociation of water and charging of the membrane surface from charged plasma states. The brief spikes in the chronoamperometric data at 3.75 and 4 V corresponded to brief interruptions in the anode water circulation.

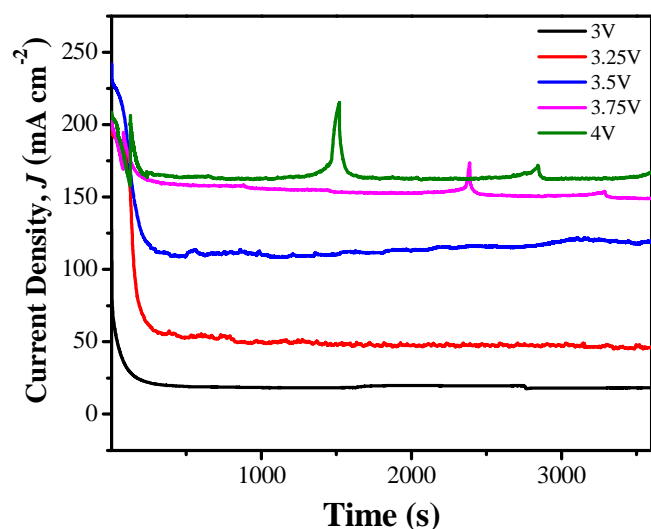


Figure S3. Current density vs. time (J - t) behavior for a constant applied bias for the electrolyzer under bias with plasma (BWP) conditions.

Energetics of Excited N_2 States and the Dissociation Barrier for Reaction

To further elucidate the proposed origin of the synergistic enhancement for ammonia formation through plasma-assisted electrochemical NRR, some simplified conceptual schematics are presented in Figure S4. Fig. S4a shows a simplified Frank-Condon diagram for nitrogen (not all energy levels and configurations are represented). Above ~ 6 eV, the N_2 molecule is sufficiently energetic to enter electronic states (e.g., $A^3\Sigma_u^+$, $B^3\Pi_g$, $C^3\Pi_u$) in which electron relaxation leads to photon emission which can be observed by optical emission spectroscopy (Fig. S1). From the ground state to ~ 6 eV, N_2 is excited through vibrational states such as the $X^1\Sigma_g^+$ system, which are not directly observable by OES. Fig. S4b shows a schematic of potential energy vs. reaction coordinate to show the N_2 excited state effect on the dissociation barrier for the reaction. Here only the first intermediate step to break the triple bond of the N_2 reactant to form two adsorbed N^* atoms at the catalyst sites is represented.³ Sufficiently energetic electronic states of N_2 (e.g., $N_2(B^3\Pi_g)$) may have enough potential energy to yield a negative change in free energy upon dissociation to adsorbed N^* and thus yield a spontaneous reaction which can produce ammonia in the presence of water. This type of route leads to NH_3 in the reactor condition for plasma with no bias (PNB). Conversely, in the bias with no plasma (BNP) operational condition, the N_2 molecules are generally in the ground state and the nitrogen dissociation reaction is energetically uphill, requiring applied potential to overcome the activation energy, E_a , to drive NRR. Nitrogen molecules in plasma-induced vibrationally excited states, $N_2^{(v)}$, on the other hand, may not have sufficient potential energy to spontaneously lead to N_2 dissociation and subsequent NH_3 formation, but these states do reduce the activation energy for NRR and thus enable additional NH_3 formation in the bias with

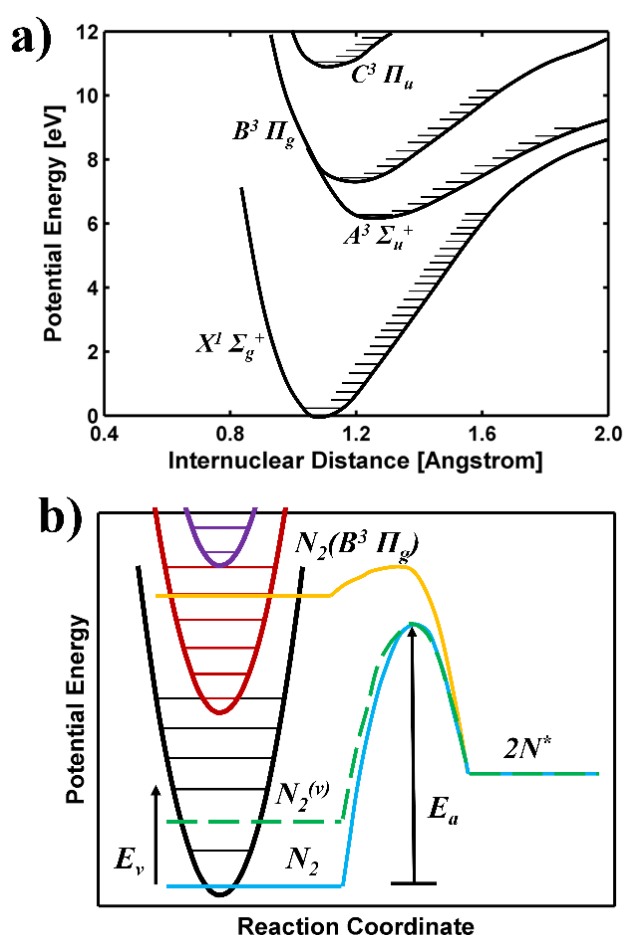


Figure S4. Schematic conceptual diagram of the energetics of excited N_2 states and the dissociation barrier for reaction. (a) Simplified Frank-Condon diagram for N_2 excited states. Vibrational states in the $X^1\Sigma_g^+$ system would not be detected by optical emission spectroscopy. (b) Schematic reaction coordinate diagram comparing activation energies (E_a) for N_2 dissociation from the ground state (blue), a vibrationally excited state (green), and an example higher excited plasma state from the $B^3\Pi_g$ system (orange).

plasma (PWB) condition that is not permitted in either PNB or BNP conditions.

Plasma-assisted Electrolyzer Stability

A practical electrolyzer for industrial use should be stable for thousands of hours. Although the PEM electrolyzer used in this work maintained its J - V performance for up to 14 h of cumulative exposure of the MEA to the N_2/He plasma, it subsequently experienced irreversible degradation. The electrolyzer J - V curves of Fig. S4 show that the current density at 3.5 V applied bias decreased 13% after 26 h of operation with plasma impinging on the cathode. The measured steady state membrane ionic conductivity did not appreciably change during this period, so we instead attribute this loss of performance to degradation of the catalyst. High-energy excited molecules and ions impacting the catalyst particles and carbon supports may induce gradual degradation via a sputtering mechanism.⁴ Improving the electrolyzer stability, by catalyst protection or an altered plasma discharge with fewer high-energy states, would be necessary to harness the plasma-assisted electrochemical process in a practical device.

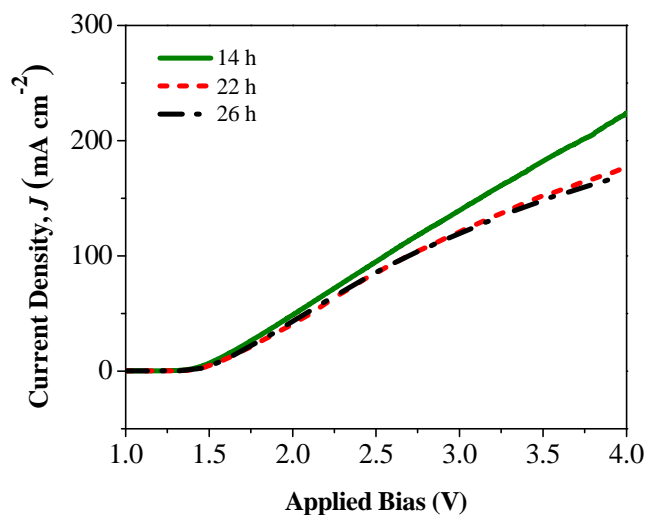


Figure S5. Current density vs. applied bias (J - V) behavior for the electrolyzer under plasma with bias conditions after cumulative exposure of the MEA to the N_2/He plasma for a time as shown in the legend. Up to 14 h, the performance was observed to be near its maximum but demonstrated decreasing performance thereafter.

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