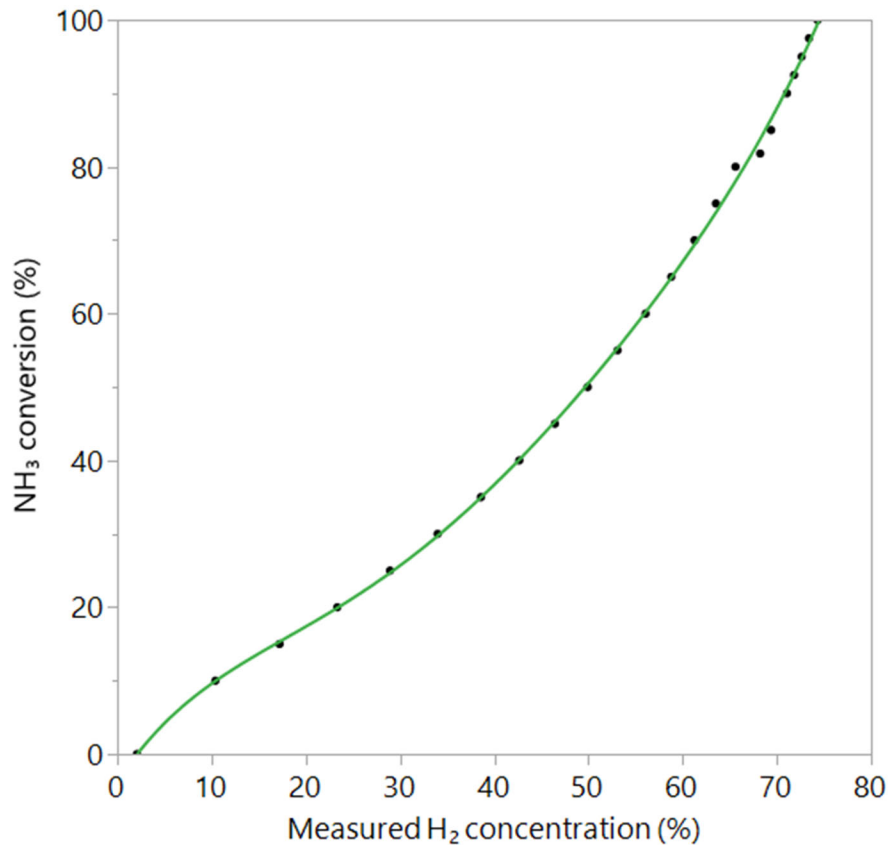


Plasma-assisted NH₃ cracking in warm plasma reactors for green H₂ production – Supporting information

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S1. Calibration curve for determining NH₃ conversion based on values measured by H₂ TCD



The calibration curve is approximated using a polynomial from equation S1.1:

$$X_{NH_3} = -25.25046 + 1.5156835 \cdot C_{H_2}^{TCD} + 0.0129463 \cdot (C_{H_2}^{TCD} - 50.1213)^2 + 5.3023 \cdot 10^{-5} \cdot (C_{H_2}^{TCD} - 50.1213)^3 + 7.1679 \cdot 10^{-6} \cdot (C_{H_2}^{TCD} - 50.1213)^4 + 1.5674 \cdot 10^{-7} \cdot (C_{H_2}^{TCD} - 50.1213)^5 \quad (S1.1)$$

where X_{NH_3} is the NH₃ conversion (in %) and $C_{H_2}^{TCD}$ is the H₂ concentration measured using the H₂ TCD.

S2. Measurement of hydrazine content in the products of NH₃ cracking

The hydrazine (N₂H₄) concentration ($C_{N_2H_4}^{out}$) in the exhaust gas was measured by scanning the samples in the 400–600 nm range using a UV/VIS spectrophotometer. The presence of N₂H₄ in the samples creates an absorbance maximum at 458 nm. The samples were prepared by dissolving NH₃ cracking products in 250 mL of deionised water (H₂O) using a gas washing bottle. 1 mL of the resulting liquid is pipetted into one quartz cuvette while a blank sample with 1 mL of deionised H₂O is prepared in the second cuvette. A N₂H₄ indicator is added to both samples. The concentration of N₂H₄ ($C_{N_2H_4}^{cuvette}$) in the cuvette sample is calculated based on the calibration formula S2.1:

$$C_{N_2H_4}^{cuvette}(\mu M) = 21.37 \cdot A + 0.15 \quad (S2.1)$$

where A is the measured absorbance at 458 nm. Equation S2.1 was obtained from the calibration of the UV/VIS spectrophotometer for defined N₂H₄ concentrations in H₂O solutions. This was done by using seven sets of standard samples with decreasing concentrations of N₂H₄ in water (Table S2.1).

Table S2.1: The measured absorbance values based on seven standards with different N₂H₄ concentrations measured with a UV/VIS spectrophotometer.

$C_{N_2H_4}^{real}$ (μM)	Absorbance (a.u.)
59.1	2.790
39.4	1.779
29.55	1.385
19.7	0.914
9.85	0.437
4.925	0.264
1.97	0.080

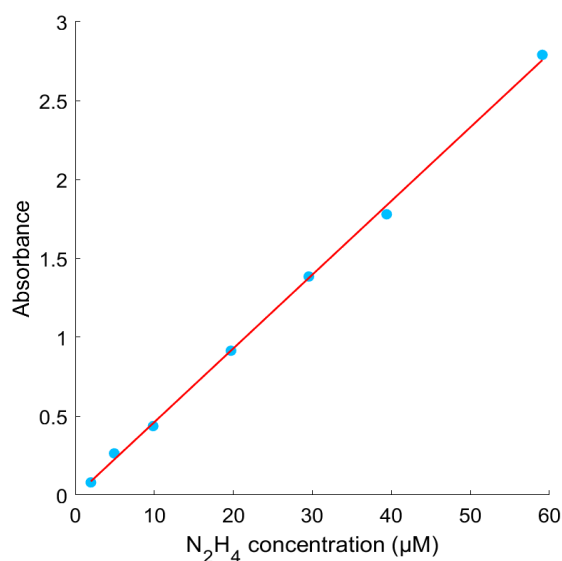


Figure S2.1. Calibration curve for UV/VIS spectrophotometer built using measured absorbance values of seven standards with different N₂H₄ concentrations.

Existing reports indicate that hydrazine production during plasma-based NH_3 decomposition is limited, so during calibration the sample with the highest concentration of N_2H_4 was prepared by dissolving 0.03 mL of a hydrazine hydrate solution (99%) in 500 mL of deionised water, after which the solution was diluted 22 times. This produces the initial sample with a hydrazine concentration of 59 μM . Six additional samples were made by diluting the first sample with deionised water 1.5, 2, 3, 6, 12 and 30 times. After an incubation time of 30 min, each sample was measured in the 400–600 nm wavelength range. A plot of the measured absorbance as a function of the real N_2H_4 concentrations (Figure S2.1) shows a linear relationship, represented by equation S2.1.

$C_{\text{N}_2\text{H}_4}^{\text{cuvette}}$ is the concentration N_2H_4 present in the cuvette sample ($V_{\text{cuvette}} = 1 \text{ mL}$). Using $C_{\text{N}_2\text{H}_4}^{\text{cuvette}}$, the total volume of liquid in the gas washing bottle ($V_{\text{GWB}} = 0.25 \text{ L}$), the total time during which the hydrazine sample was collected (t_{sample}), and molar volume of gaseous hydrazine ($V_m = 22.4 \text{ Ln/min}$), we can calculate the flow rate of hydrazine in the cracking products ($Q_{\text{N}_2\text{H}_4}^{\text{out}}$) via equation S2.2.

$$Q_{\text{N}_2\text{H}_4}^{\text{out}} \left(\frac{\text{Ln}}{\text{min}} \right) = \frac{C_{\text{N}_2\text{H}_4}^{\text{cuvette}} \left(\frac{\text{mol}}{\text{L}} \right) \cdot V_{\text{GWB}} (\text{L}) \cdot V_m \left(\frac{\text{Ln}}{\text{mol}} \right)}{t_{\text{sample}} (\text{min})} \quad (\text{S2.2})$$

By knowing the composition of cracking products, we can calculate their total flow rate ($Q_{\text{total}}^{\text{out}}$) and then use it and $Q_{\text{N}_2\text{H}_4}^{\text{out}}$ to find $C_{\text{N}_2\text{H}_4}^{\text{out}}$ using formula S2.3.

$$C_{\text{N}_2\text{H}_4}^{\text{out}} = \frac{Q_{\text{N}_2\text{H}_4}^{\text{out}}}{Q_{\text{total}}^{\text{out}}} \quad (\text{S2.3})$$

A solution of NH_3 decomposition products that was used for hydrazine measurement was produced by passing the output gas at a set gas flow rate through a gas washing bottle for $t_{\text{sample}} = 30 \text{ min}$. The analysis of the obtained solution shows that the hydrazine concentration in the NH_3 decomposition products was less than 0.0003 %. This supports our initial assumption upon which the composition of decomposition products is measured: the decomposition of NH_3 results in a mixture of H_2 and N_2 with a ratio of 3:1 with insignificant concentration of byproducts, such as hydrazine.

S3. Estimation of the rotational temperature using OES

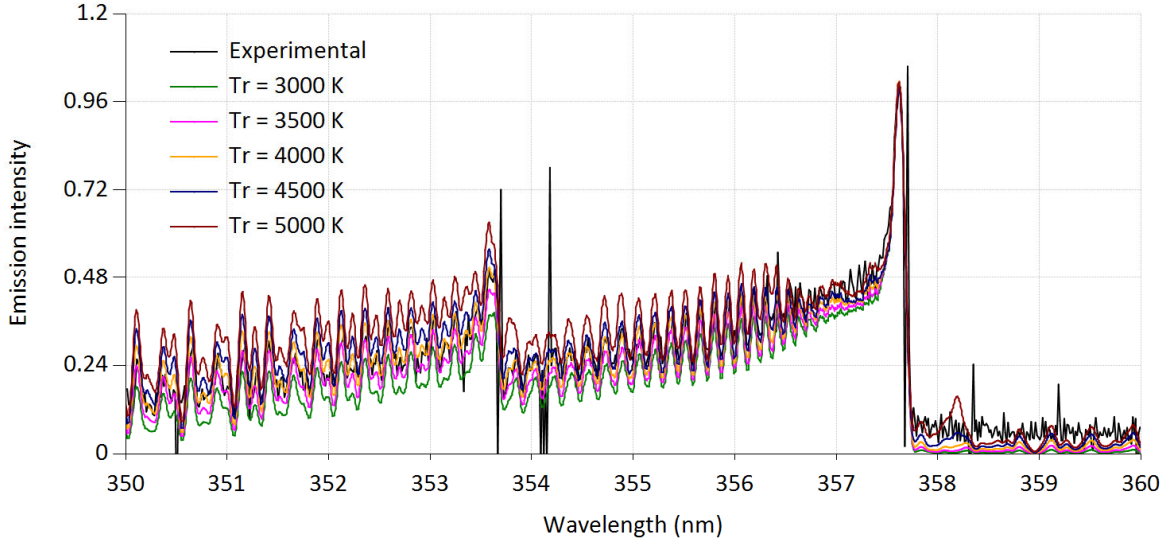


Figure S3.1. Example of SpecAir simulation of the P2P arc discharge spectrum obtained at a current of 140 mA, feed flow rate of 20 Ln/min and SEI of 68.9 kJ/mol.

Figure S3.1 illustrates the measured OES spectrum for the P2P arc discharge, as well as some simulated spectra for different rotational temperatures (see legend). The simulated spectra in the T_{rot} range from 3500 to 4500 K provided more or less the same good fit to the experimental spectrum. At T_{rot} below 3500 K and over 4500 K, the fit was significantly worse. Hence, we estimate $T_{rot} = 4000 \pm 500$ K as the gas temperature inside the core of the arc plasma channel.

S4. Thermodynamic calculations

Figure 9 in the main paper was made by finding the chemical composition at a specific temperature that minimizes the Gibbs free energy. The calculations were performed using the free software Cantera [1]. The Gibbs free energy is calculated based on the NASA9 polynomials [2] and minimized using the VCS algorithm [3].

The mixture is initialized at a specific temperature, pressure, and chemical composition. It is then equilibrated at this temperature and pressure. Based on the equilibrium composition, the energy cost (EC) is then given by equation (S4.1)

$$EC \left(\frac{kJ}{mol} \right) = \frac{\Delta H}{X} = \frac{H(T) - H(T_0)}{X} = \frac{\sum H_i(T) y_i - H_{NH_3}(T_0)}{X} \quad (S4.1)$$

Where the sum runs over all species in the mixture and y_i is the mole fraction of the i -th species. The initial enthalpy is given by the enthalpy of ammonia at the reference temperature of 273.15 K. The conversion X is calculated by equation (4) in the main paper.

Figure 10 in the main paper is calculated by defining the specific energy input (SEI) as the change in enthalpy and plotting the corresponding temperature. This will always give a monotone increasing function since heat capacities are always non-negative [4].

The species present in the mixture are e^- , H, H^+ , H_2 , H_2^+ , N, N^+ , N_2 , N_2^+ , N_3 , NH, NH^+ , NH_2 , NH_3 , NH_4^+ , N_2H_2 , and N_2H_4 . These are all the dominant neutral and positive ion species, and the electron.

The composition as a function of temperature is presented in figure S4.1.

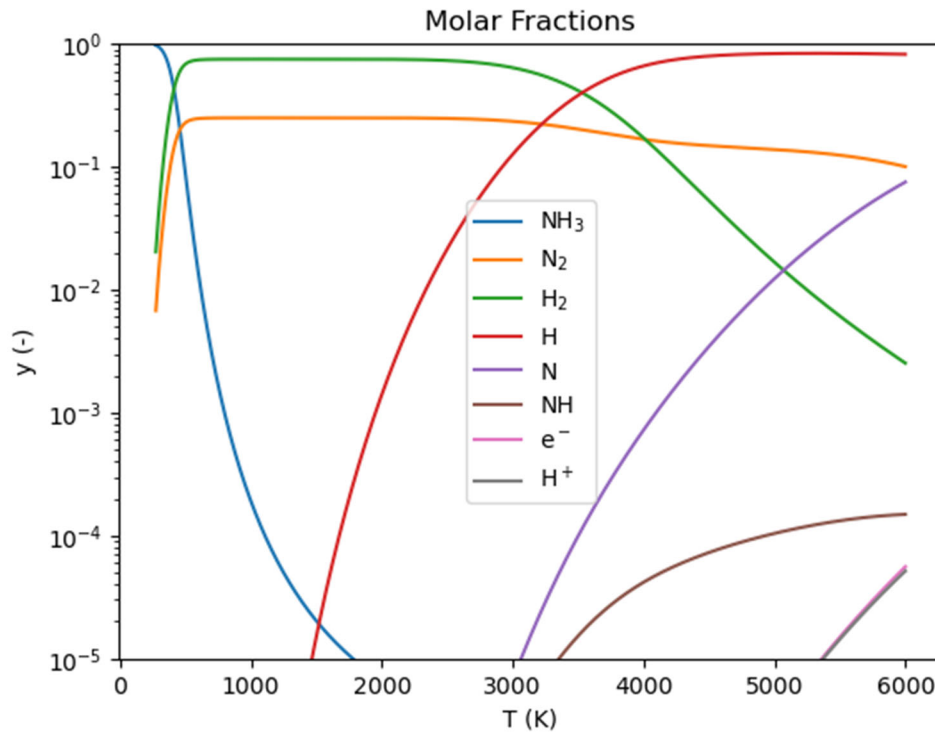


Figure S4.1 Calculated molar fractions for the species with maximal molar fraction over 10^{-5} . The legend shows what color corresponds to which species.

References

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