

Supplementary Information

Disproportionation of nitrogen induced by DC plasma-driven electrolysis in a nitrogen atmosphere

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

Detailed descriptions of experimental procedures

("Normal conditions" group)

- First, the vessel is pumped down to 50 mTorr in order to remove residual gas and impurities
- Nitrogen gas is injected into the chamber (1slm), the pump is switched off and the pressure inside the chamber is brought to atmospheric pressure
- The pump is switched on again to decrease the pressure below 50mTorr and off again to bring the pressure back to atmospheric pressure using the nitrogen gas flow, two more times
- The outlet gas flow is then directed through the exhaust bubbler (50ml of fresh milli-Q water)
- The 50ml of water + NaCl (1 mM) is injected into the chamber, inside the beaker, through a septum
- The temperature and relative humidity inside the vessel are recorded and the amount (in mol%) of water vapor is calculated
- When the initial water content stabilizes below 1 mol% (0.8-1 mol% in average), the gas discharge is ignited for 30min

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- One high resolution optical emission spectra is recorded during the plasma treatment
- After 30min, the plasma-driven electrolysis is switched off, the treated water from the beaker inside the vessel is immediately sampled (using a syringe through a septum) for analysis (Liquid chromatography, pH, colorimetry assays and UV-Vis spectrophotometry) while the nitrogen gas flow remains running through the chamber and the exhaust bubbler to flush every gaseous species through it
- After 15 more minutes, the nitrogen gas flow is stopped and the exhaust bubbler water is sampled for analysis (Liquid chromatography, pH, colorimetry assays and UV-Vis spectrophotometry)

Detailed descriptions of experimental procedures

("H₂O admixtures" group)

- First, the heating system is switched on for one hour, in order to stabilize its temperature at 67°C (vessel, gas lines and humidifier bubbler, filled with 250ml of fresh milli-Q water)
- The vessel is pumped down to 50 mTorr in order to remove residual gas and impurities
- Nitrogen gas is injected into the chamber (1slm), the pump is switched off and the pressure inside the chamber is brought to atmospheric pressure
- The pump is switched on again to decrease the pressure below 50mTorr and off again to bring the pressure back to

atmospheric pressure using the nitrogen gas flow, two more times

- The inlet gas flow is then directed through the humidifier inlet bubbler
- The outlet gas flow is directed through the exhaust bubbler (50ml of fresh milli-Q water)
- The 50ml of water + NaCl (1 mM) is injected into the chamber, inside the beaker, through a septum
- The temperature and relative humidity inside the vessel are recorded and the amount (in mol%) of water vapor is calculated
- The gas discharge is immediately ignited for 30min, after verification that the initial water vapor ranges from 6 to 8 mol%
- One high resolution optical emission spectra is recorded during the plasma treatment
- After 30min, the plasma-driven electrolysis is switched off, the treated water from the beaker inside the vessel is immediately sampled (using a syringe through a septum) for analysis (Liquid chromatography, pH, colorimetry assays and UV-Vis spectrophotometry) while the nitrogen gas flow remains running through the chamber and the exhaust bubbler to flush every gaseous species through it
- After 15 more minutes, the nitrogen gas flow is stopped and the exhaust bubbler water is sampled for analysis (Liquid chromatography, pH, colorimetry assays and UV-Vis spectrophotometry)

Calculation of the conversion rate of nitrogen

The conversion rate of N_2 was calculated as the ratio of the depleted nitrogen to the injected nitrogen during the whole process ($t = 30\text{min}$):

$$X_{N_2} = \frac{n_{N_2 (mol)} (depleted)}{n_{N_2 (mol)} (injected)}$$

In order to perform this calculation, two assumptions were considered:

- 1) One mole of depleted nitrogen provides two moles of fixed nitrogen (in the form of molecules and ions containing one nitrogen atom)
- 2) All depleted nitrogen reacted to form a stable species which was subsequently measured

Thereafter, the total amount (in mole) of fixed nitrogen was divided by two and considered equal to the amount (in mole) of depleted nitrogen.

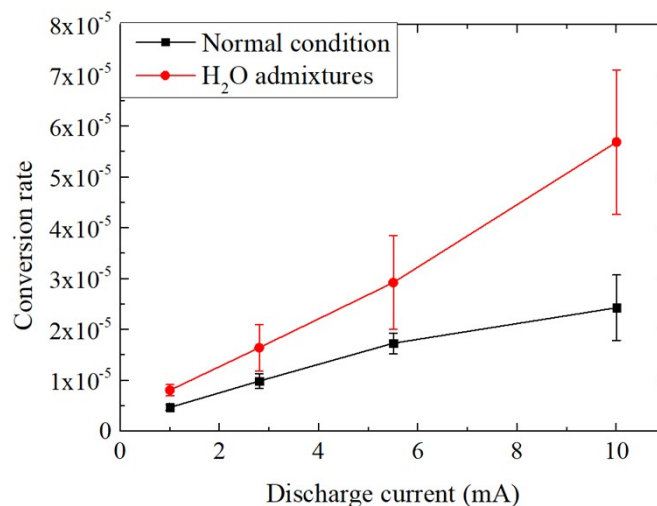


Figure 1: Conversion rate of nitrogen as a function of the N_2 plasma-electrolysis current, for the two experimental groups.

Data Analysis

All the plasma-electrolysis experiments were repeated 3 times, along with all the corresponding analysis (Optical emission spectroscopy, Liquid chromatography, colorimetry, pH). Quantitative values presented are averaged from the three measurements and error bars correspond to the standard deviation.

Spectrometer calibration

The spectrometer was calibrated using a calibrated quartz tungsten halogen light source¹. 3 spectra of the lamp emission were recorded using the Andor SR-500i-D2-R spectrometer with an Andor DU420 CCD camera with an opened electrode, through its optical fiber. For each spectrum, 10 acquisitions of 10 μs were carried out, for a total exposure time of 100 μs . A 2400 grooves/mm grating was used to

record spectra in the spectral range 200-700nm, with a resolution of 0.0176nm. The entrance slit was 160 μ m.

The three acquired spectra of the quartz tungsten halogen light source were background corrected and averaged (Figure 2) and the correction function of the spectrometer (Figure 4) was determined by dividing the spectral radiance of the lamp (Figure 3) by its acquisition (Figure 2).

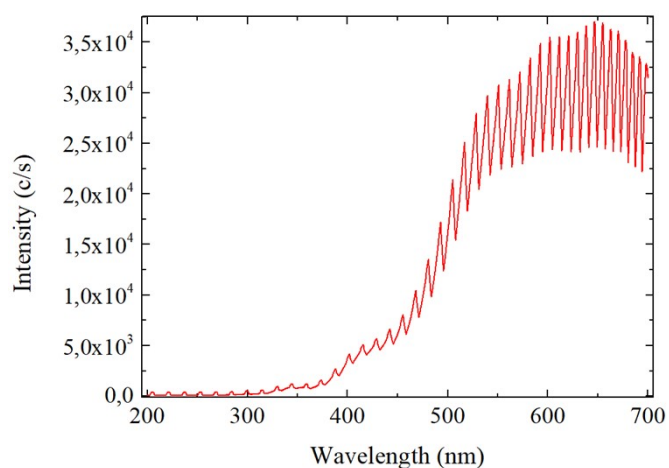


Figure 2: Averaged spectrum (background corrected) of the calibrated quartz tungsten halogen light source used for the absolute calibration of the the Andor SR-500i-D2-R spectrometer

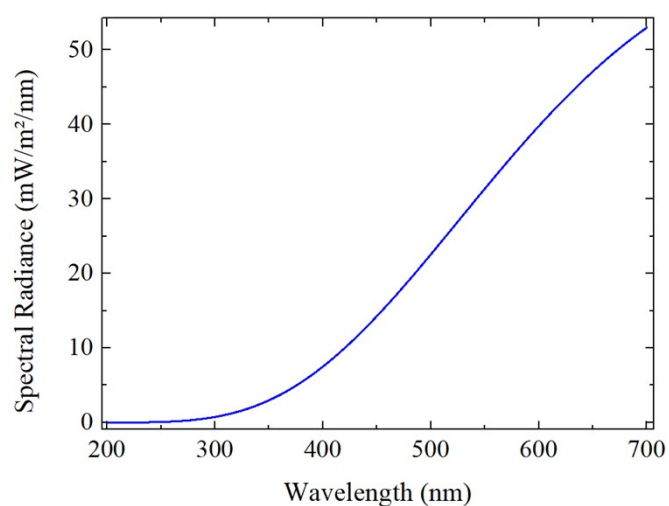


Figure 3: spectral radiance of the calibrated quartz tungsten halogen lamp used for the absolute calibration of the the Andor SR-500i-D2-R spectrometer

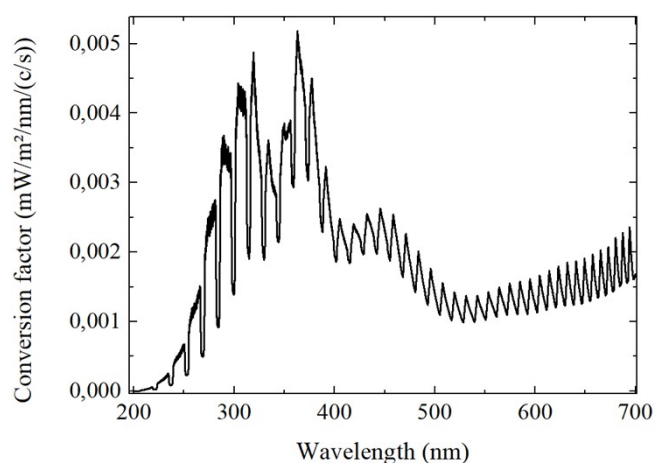


Figure 4: correction function of the spectrometer / optical fiber system using a 2400 grooves/mm grating

Following the calibration, each (background corrected) emission spectrum of the plasma was multiplied by the correction function of the spectrometer, leading to a light emission in mW/m²/nm. These absolutely calibrated spectra were subsequently used for the determination of T_{rot} and T_{vib} .

- 1 H. Lee, C. Oh and J. W. Hahn, *Propellants Explos. Pyrotech.*, 2012, **37**, 116–121.