Scaling up energy-efficient plasma-based nitrogen fixation: Supporting Information

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1. Actual pictures of the small and large reactor

Figure S1 illustrates the actual pictures of small and large reactors that are used in our experiments. Note that the large reactor in torch configuration looks the same as the pin-to-pin reactor from the outside, because the reactor is not transparent. The difference inside is illustrated by the schematic representation in Figure S2.

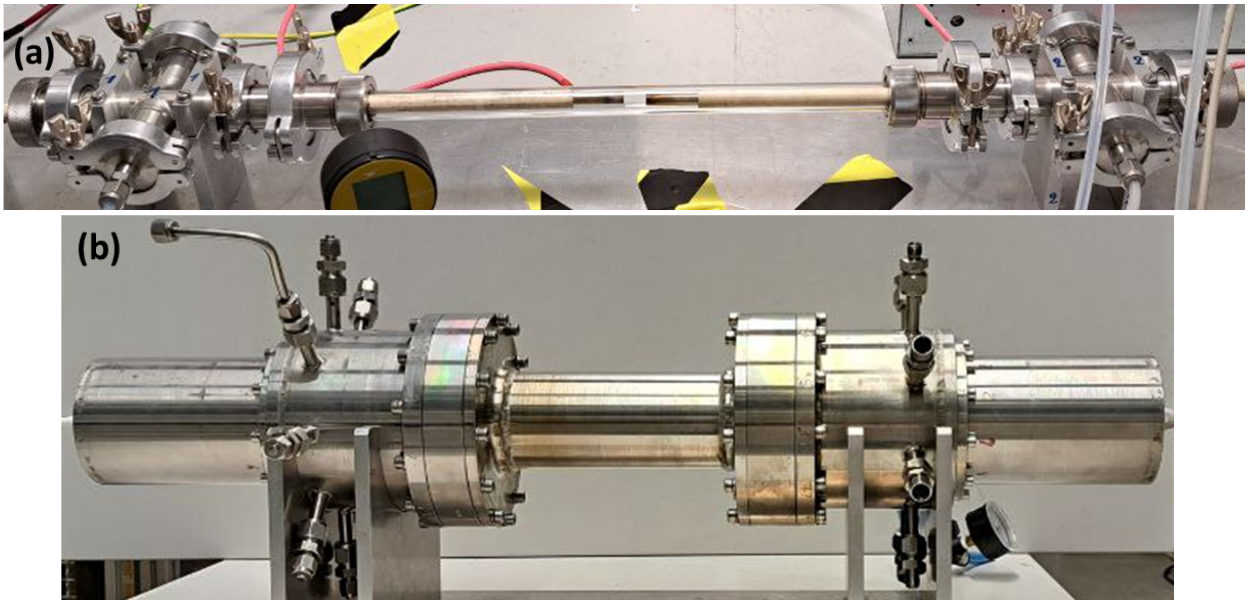

Figure S1. Actual pictures of (a) small and (b) large reactor.

2. Calibration procedure of the NDIR

Diagnostic device is an integral part of each experimental setup that is used for gas conversion purposes. In our experiments with the small reactor, we used a non-dispersive infrared (NDIR) analyzer (EMERSON-Rosemount X-STREAM enhanced XEGP) to measure the amount of NO_x (i.e., NO and NO_2) in the downstream gas flow mixture that exists the reactor. Considering a linear relationship for the measured concentrations by such a device is far from expectation. Therefore, to obtain the most reliable and accurate measurement results, NDIR requires regular calibration following three steps that are explained below.

Zero calibration: This step includes the introduction of a pure gas stream, which is typically the background gas that is recommended by the manufacturer (nitrogen in our case), to device, and the displayed value by the NDIR forms the lower limit of the calibration curve as presented in Figure S2 a and b for NO and NO_2, respectively.

Span calibration: In this step a gas mixture containing the targeted gases (NO and NO_2 in our case), with a concentration range between 80 to 110% of the maximum measurement limit of the NDIR enters the device, and the value measured by the NDIR forms the upper limit of the calibration curve.

Generation of the calibration curve: in this step several gas mixtures with various concentrations of the targeted gas between the lower and upper limits of the device are introduced to the system, and measured values by the NDIR are recorded as a function of the actual gas mixture that is fed to the system. Finally, by plotting the actual concentrations of the gas mixture as function of the read values from the NDIR, and performing a 4^{th} order polynomial regression, a standard correlation can be obtained to measure accurate concentrations of NO and NO_2 exiting the reactor.

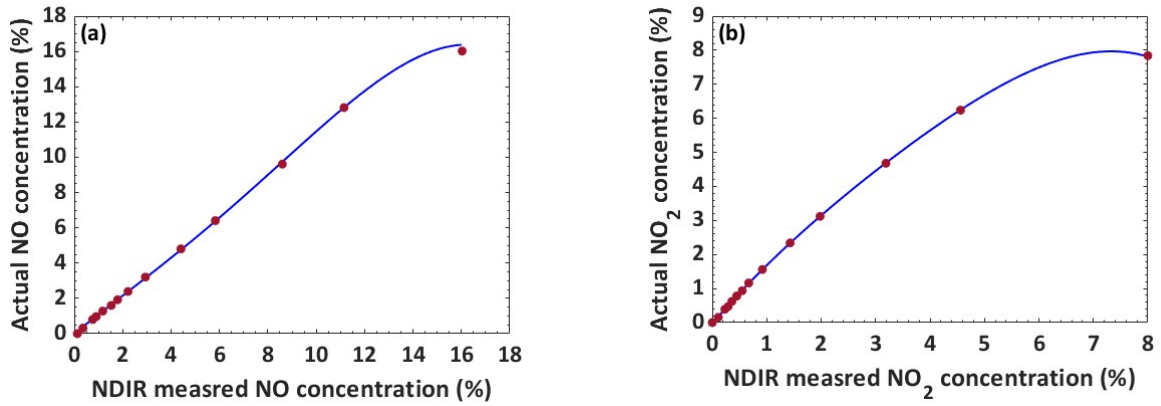

Figure S2. Calibration curves of the NDIR generated for measuring the actual concentrations of a) NO and b) NO_2.

3. Large reactor in torch configuration

A schematic of the large reactor in torch configuration is presented in figure S3. The reactor setup was the same as in pin-to-pin configuration, except that the bottom electrode was removed, and the reactor body acted as the grounded electrode. Therefore, when the gas breaks down due to the applied voltage of 10 kV by the power supply, a plasma forms between the electrode and the reactor body.

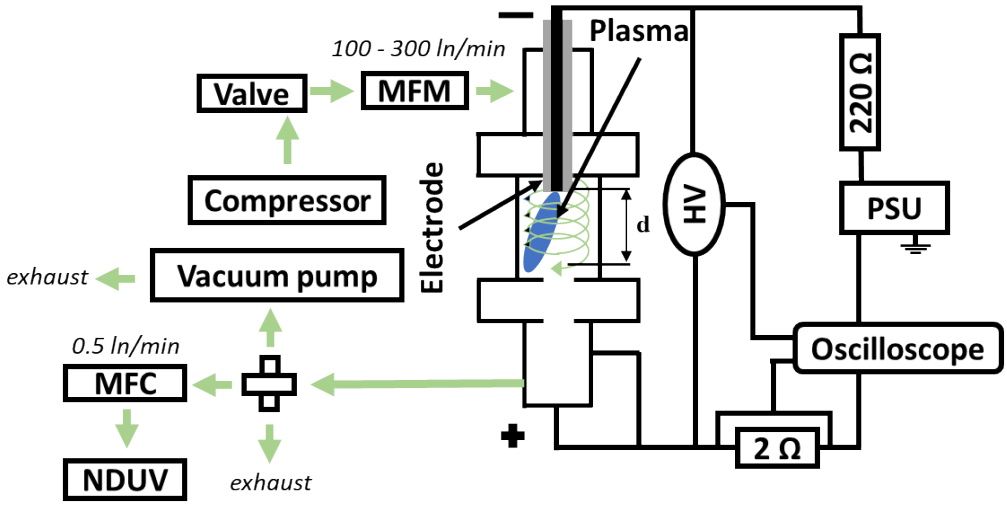

Figure S3. Schematic representation of the large reactor in torch configuration, with plasma (indicated in blue) ignited between the electrode (indicated in black) and the reactor body, and the swirling flow around the plasma (indicated in green).

4. Voltage-Current characteristics for the small and large reactor

The temporal behaviour of plasma voltage and current for the small reactor and its larger counterpart in the pin-to-pin and torch configuration are shown in Figure S4.a-d. Applying a potential difference of about 10 kV in between the electrodes, results in the gas breakdown and formation of an arc discharge in the space between the electrodes (or between the electrode and the reactor body, for the torch configuration) which starts to glide along the exposed part of the electrode. While the arc is gliding, energy is dissipated into heat and radiation (cf. figure 5 of the main paper). In the small reactor, despite that a rather stable plasma was observed, the voltage and current are periodically oscillating around the current value set on the power supply (Figure S4.a-b). For the large reactor in pin-to-pin configuration, we observed a rather random behaviour with longer periods of stability. Again, the voltage and current are oscillating around the mean voltage value and the set current value on the power supply (Figure S4.c), however, these oscillations are stronger than for its smaller counterpart. For the large reactor in torch configuration, the fluctuation of voltage and current is less pronounced than in pin-to-pin configuration, but still a random behaviour of stability periods was observed (Figure S4.d). These relatively strong oscillations of the voltage and current as a function of time, together with the random behaviour of stability periods, indicate that the large reactor, in both pin-to-pin and torch configuration, is operating in a restriking regime [1,2].

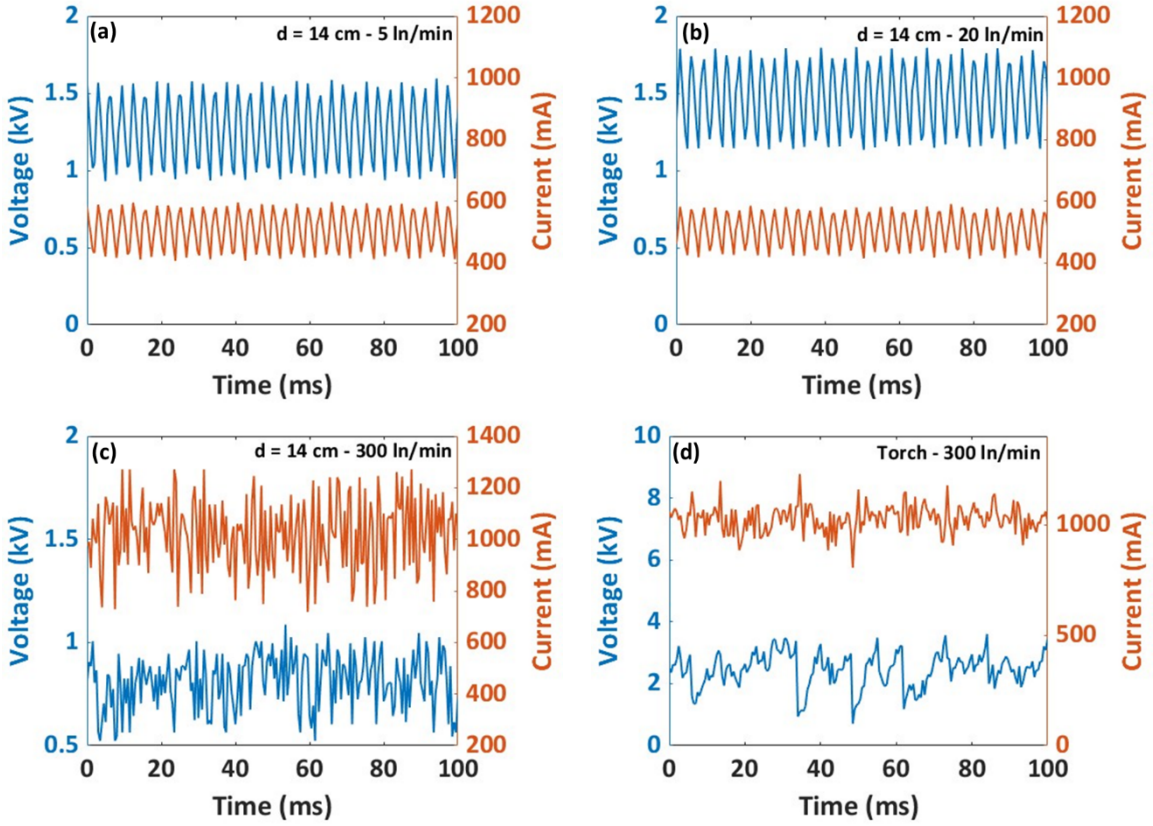

Figure S4. Temporal behaviour of plasma voltage and current for a distance between the electrodes of 14 cm, in the small reactor operating at 5 and 20 ln/min and applied current of 500 mA (a and b, respectively), the large reactor in pin-to-pin configuration (c), and in torch configuration (d), both at 300 ln/min and applied current of 1000 mA.

5. EC and NO_x concentration in the large reactor without swirling flow

The EC and NO_x concentration in the large reactor in pin-to-pin configuration without swirling flow are plotted as a function of SEI in Figure S5, for three different flow rates and two distances between the electrodes. The highest NO_x concentration is 0.25%, obtained at the highest SEI, and corresponds to an EC of 4.8 MJ/mol. A lower EC of 3.3 MJ/mol was obtained at a lower SEI of 0.26 kJ/l, but the corresponding NO_x concentration here is only 0.19%. While the NO_x concentrations are slightly higher than in the same reactor with swirling flow (where a maximum value of 0.21% is obtained, see Figure 9 b and Figure 10 b in the main paper), the EC is somewhat worse (i.e., the lowest EC obtained in the reactor with swirling flow was 2.9 MJ/mol; Figure 10 a in the main paper). This indicates that the swirling flow helps to not only improve the plasma stability, but also the reactor performance in terms of EC.

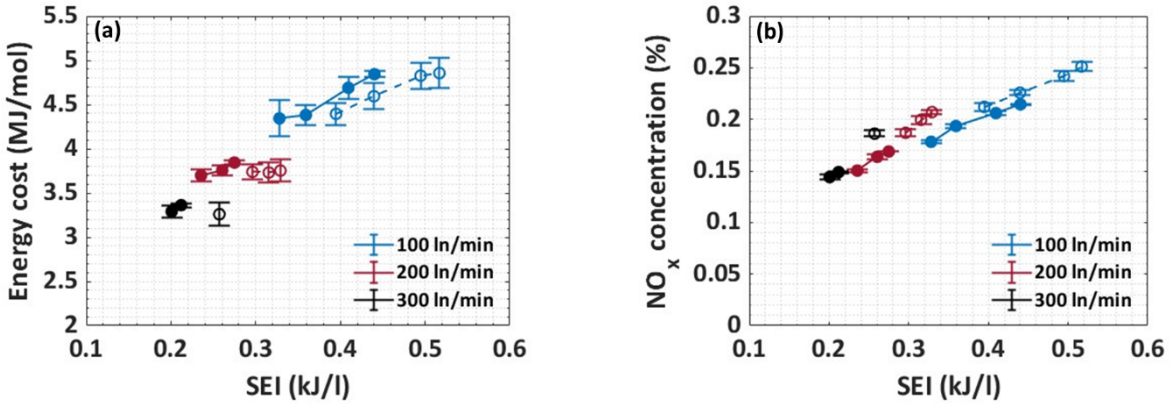

Figure S5. EC (a) and NO_x concentration (b) in the large reactor in pin-to-pin configuration without swirling flow, as a function of SEI, for three different flow rates and two distances between the electrodes (dashed lines/open symbols, and solid lines/closed symbols, for d = 7 and 14 cm, respectively). Error bars are indicated but are often too small to be visible.

References

1 S. A. Wutzke;, E. Pfender; and E. R. G. Eckert;, *AIAA J.*, 1967, **5**, 707–713.

2 J. P. Trelles, E. Pfender and J. Heberlein, *Plasma Chem. Plasma Process.*, 2006, **26**, 557–575.