

Lifetime of Nitric Oxide Produced by a Surface DBD in Controlled Atmospheres

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Abstract: Atmospheric plasmas have been known to generate high-purity and high-concentration nitric oxide (NO), but the lifespan of NO in plasma, which is strongly affected by ambient conditions, is still unclear. Here, we investigate dynamics of NO in a surface dielectric barrier discharge reactor, and its lifetime is determined under NO-rich conditions according to O₂ content in the reactor. As O₂ was reduced in the plasma reactor, maximum concentration of NO decreased but reached fast, and its lifetime was extended significantly.

Keywords: Surface Dielectric Barrier Discharge, Nitric Oxide (NO), UV-visible absorption spectroscopy

1. Introduction

Nitric oxide (NO) is an important molecule from in nature and the human body to for anthropogenic chemicals. For example, nitric oxide is an air-cleansing molecule¹ and plays an invaluable role in the blood pressure, neurotransmission and immune system of the human body². Inhaled NO therapy can be used for managing adult respiratory distress syndrome³, and recently Kobayashi and Murata⁴ reported that nitric oxide has the potential to be of therapeutic value in COVID-19 patients. One of the interesting implications of NO is the suppression of fruit ripening and the resultant shelf-life extension^{5,6}.

For practical usage of NO in certain applications including the foregoing examples, costly and cumbersome gas cylinders are not favored. There have thus been increasing demands for a compact, on-site source of nitric oxide with a high purity and high reliability, and several methods have been developed.

Meanwhile, atmospheric plasmas have been (re)emerging for green chemistry and agri-food applications because of their unique feature of chemistry pertaining to abundant reactive oxygen and nitrogen species (RONS). Regarding NO production in plasmas, increasing attention has been paid to several types of plasma operated in the air, and previous works have demonstrated attractive ways to make plasma seem as a reliable NO source^{7,8}. However, given that NO is rapidly oxidized by O₂ and/or O₃, NO produced in air discharges is naturally unpractical, and the lifetime of NO therein remains uncertain thus far.

In this study, we examined the time development of ozone (O₃) and nitrogen oxides (NO_x) in a surface dielectric barrier discharge (sDBD) reactor depending on O₂ content of controlled atmosphere (N₂ + O₂). To quantify O₃ and NO_x without loss, an *in situ* optical absorption spectroscopy was employed. With decreasing the O₂ content in the plasma reactor, maximum

concentration of NO decreased, but the significant increase in its lifetime was observed. In addition, we found that the lower the O₂ ratio, the faster the transition of the dominant chemical from O₃ to NO in the plasma reactor.

2. Experimental setup

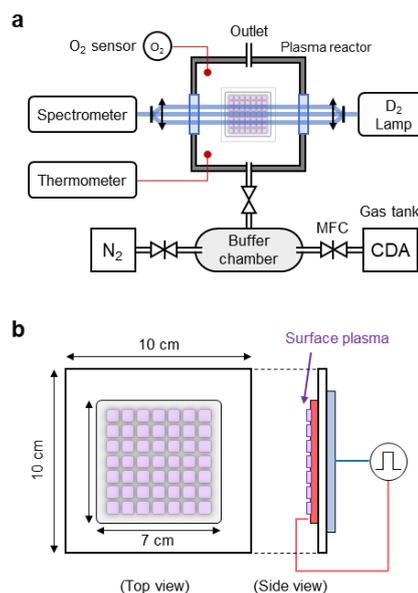


Fig. 1. (a) Simplified drawing of our experimental setup involving a plasma reactor equipped with an *in situ* absorption spectroscopy system. Controlled atmospheres were made by adjusting flow rates of N₂ and CDA, (b) Top and side-view illustration of the sDBD source with an electrical connection to the power supply.

A schematic of the experimental apparatus used in this study is presented in Fig. 1a. A gas-tight stainless-steel chamber was utilized as a plasma reactor with an sDBD source that comprise one of the chamber walls. The sDBD source is composed of a 1-mm-thick 10×10 cm² fused

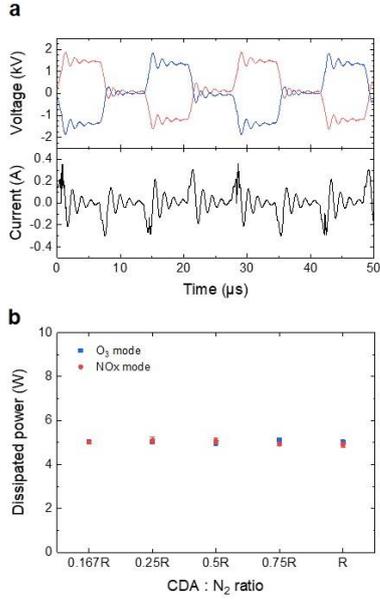


Fig. 1. (a) Voltage (upper panel) applied to the sDBD source in CDA and the resultant current waveform (bottom). (b) Time-averaged electric power dissipated in the sDBDs.

silica plate with two 7×7 cm² thin film electrodes attached to each side. One of the electrodes has rounded, 7×7 mm² square holes in a 7×7 arrangement, thereby producing the air surface discharges at the open edges (see Fig. 1b). Both electrodes were connected to a high-voltage power source (FTLAB HPI500), supplying bipolar square voltage waveforms with opposite polarities to each electrode. The driving frequency was set at 40 kHz with a duty cycle of 25% (see Fig. 2a). Flow rates of clean dry air (CDA) and N₂ were controlled by using mass flow controllers (ISVT IMC1300). The voltage and current waveforms of sDBD were recorded on a digital oscilloscope (Tektronix MDO34) using a high-voltage probe (Tektronix P6015A) and a current probe (Pearson Electronics Model-4936).

Two fused silica windows on either side of the chamber allowed to use *in-situ* UV-visible absorption spectroscopy. A combination of a halogen-deuterium lamp (Ocean Insight DH-mini) and a spectrometer (Ocean Insight Maya2000 Pro) was aligned through an absorption path length of 150 mm, as seen in Fig. 1a. Two optical fibers (Ocean Insight QP400-2-SR) and two collimating lenses (Ocean Insight 74-UV) were used to transmit and collimate the lamp light through the chamber and into the spectrometer. All spectral data were automatically acquired with a time interval of 500 ms, and absolute number densities of chemical species were obtained based on the Beer-Lambert law.

Prior to every experiment, the atmospheric condition of the plasma reactor was changed by simultaneously supplying CDA and N₂ gases. According to the different ratios of gas flow rates, we created O₂ levels ranging from 3.3% to 21% (CDA) in the reactor, hereinafter defined as 0.167R – R. To ensure a stationary environment, both

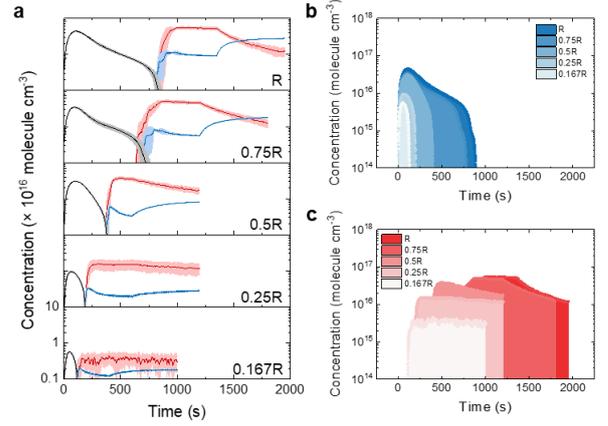


Fig. 3. Time development of O₃ (black), NO (red), and NO₂ (blue) with different O₂ contents in the plasma reactor. Data of (b) O₃ and (c) NO extracted from (a) is replotted.

gases were flowing enough for up to 10 minutes with a CDA flow rate of 1 standard liter per minute, and intended O₂ percentages were confirmed using an oxygen sensor. Note that time-averaged power dissipated in the sDBD source remains nearly constant at approximately 5 watts, regardless of the CDA:N₂ ratio (Fig. 2b).

During the measurements, we observed the chemical mode transition from O₃ to NO in all cases, albeit the different lengths of time taken. When the concentration of nitric oxide is saturated in the plasma reactor, plasmas were turned off, and post-discharge measurements were then continued for 10 minutes to assess NO lifetime. Each experiment was repeated three times in the same condition without any replacement.

3. Results and Discussion

The time development of NO, NO₂, and O₃ concentrations inside the chamber varied depending on the oxygen ratio (Fig. 3a). The time at which the plasma was generated was set at 0 in the figure. In all cases, ozone appeared first at the beginning of plasma-on time, but soon NO prevailed in the reactor.

For the sake of comparison, the temporal behaviors of the O₃ and NO in the different oxygen concentrations are

Table 1. Specific values of data presented in Fig. 3a.

CDA:N ₂		R	0.75R	0.5R	0.25R	0.167R
Post discharge	O _{3,max} [10 ¹⁵ cm ⁻³]	51.4	34.6	30.5	9.57	5.69
	NO ^{max} [10 ¹⁵ cm ⁻³]	51.4	45.9	35.2	15.3	4.58
	NO ^{min} [10 ¹⁵ cm ⁻³]	12.5	12.9	17.0	11.7	3.13
T _{trans} [s]		893	789	403	203	133

replotted in Fig. 3b and 3c, respectively. The maximum concentration of O₃ is proportional to the oxygen ratio (Table 1). According to the reaction $O + O_2 + M \rightarrow O_3 +$

M (where M is the third body), ozone is mainly originated from atomic oxygen reacting with O_2 . Thus, the results imply that the production of atomic O was somehow reduced in the sDBD along with decreasing O_2 ratio.

Again, in all cases, NO and NO_2 began to predominate over O_3 after certain discharge periods, defined as the transition time T_{trans} of the chemical mode from O_3 to NO. In CDA, the time T_{trans} was 893 s, and T_{trans} becomes faster with decreasing the O_2 ratio (corresponding to increased N_2). One possible reason for this feature is that the higher vibrational temperature and the larger concentration of excited $N_2(v)$ as O_2 is reduced, the more atomic O is turned into NO rather than into O_3 via $O + N_2(v) \rightarrow NO + N$.

NO and NO_2 produced in the plasma reactor were also monitored during the post-discharge period (10 min). As shown in Fig. 3a, NO decayed rapidly, whereas NO_2 is continuously produced, despite turning off the plasma. Although a highly oxidative species, e.g. O_3 , is absent, NO is readily oxidized by abundant O_2 in the plasma reactor: $2NO + O_2 \rightarrow 2NO_2$.

4. Conclusion

The dynamics and lifetime of NO according to the O_2 contents of controlled atmosphere were studied based on the model experiment. We found that the chemical mode transition time was changed because oxygen ratio is crucial in the production of both O_3 and NO_x in the reactor. Although NO dominantly reacts with O_2 ($2NO + O_2 \rightarrow 2NO_2$), the decay of NO concentration seems to be nonlinearly proportional to the O_2 concentration. A future study relevant to chemical modelling will seek to provide further understanding of this nonlinear result.

To summarize, the decrease in oxygen concentration in the sDBD reactor leads to the fast transition of chemical mode and increase in the NO lifetime. Our findings indicate that appropriate control of oxygen content is essential in atmospheric plasma reactors depending on O_3 and/or NO_x applications. Moreover, the results reveal that atmospheric plasmas can be utilized as one of the promising sources of NO in various applications of interest.

5. References

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Acknowledgments

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