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Ozone-free nitric oxide production using an atmospheric pressure surface discharge – A way to minimize nitrogen dioxide co-production

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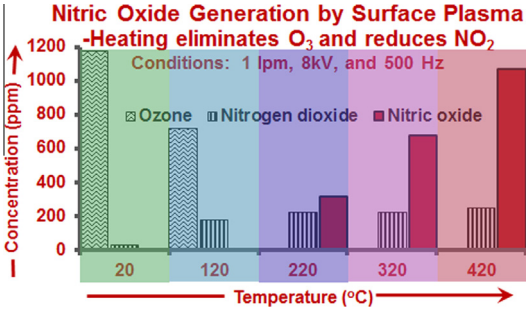
HIGHLIGHTS

- Nitric oxide generator based on surface discharge in atmospheric pressure.
- Energy deposition increased significantly with increase in surface temperature.
- Energy yield for nitric oxide production increased with increase in temperature.
- NO/NO_2 ratio increased from 1.5 at $\geqslant$220 °C to more than 4 at 420 °C without O_3.

GRAPHICAL ABSTRACT



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ABSTRACT

Effects of temperature on nitric oxide (NO) production and on byproduct nitrogen dioxide (NO_2) and ozone (O_3) in a non-equilibrium sliding discharge in atmospheric pressure air are described. Heating the electrodes/dielectric surfaces in contact with the discharge plasma from 20 °C to 420 °C caused an increase in energy per pulse by more than an order of magnitude. More importantly, heating to a few hundred degrees above room temperature caused the destruction of ozone (O_3) and the reduction of nitrogen dioxide (NO_2) but promoted NO formation. At 20 °C, 400–4500 ppm O_3 with an energy cost of 2–4 MJ/mol, and 12–180 ppm NO_2 with an energy cost of 75–140 MJ/mol were generated from dry air flowing at 1 lpm. At 220 °C, however, NO and NO_2 were produced in about equal proportion while O_3 was below detection limits. The efficiency of NO generation increased with an increase of temperature. At the maximum temperature used in this study, i.e., 420 °C, 160–1040 ppm NO was produced from dry air at an energy cost of 24–67 MJ/mol, with a NO/NO_2 ratio of more than 4 and free of O_3.

1. Introduction

Nitric oxide (NO) is a universal anti-microbial antihypertensive and also works as a pulmonary vasoregulator [1–7]. Applications range from wound disinfection/healing to inhalation therapy for some lung diseases. Conventionally, NO is supplied from nitrogen gas cylinders containing a high concentration of NO. The gas cylinders are expensive, not easily portable and associated with a risk of gas leakage that may convert NO into more toxic nitrogen dioxide (NO_2). Therefore, less expensive, safer, portable and on-site NO production devices based on plasma technologies are being developed [6–19].

These plasmas are formed by high voltage electrical discharges where energetic electrons are produced and collide with ambient gas molecules to form the desired species via direct and indirect electron impact processes and chemical reactions. For example, the dissociation of N_2 and O_2 into N and O, respectively, or the

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excitation of these molecules may lead to synthesis of new reactive oxygen species and reactive nitrogen species such as ozone (O_3) and NO via the following reaction channels [20–22]:

$$e^* + O_2 \rightarrow e + 2O, \quad (1)$$

$$O + O_2 + M \rightarrow O_3^* + M \rightarrow O_3 + M, \quad (2)$$

$$e^* + N_2 \rightarrow e + N + N^*, \quad (3)$$

$$N^* + O_2 \rightarrow NO + O, \quad (4)$$

where * represents an excited state, e^* represents a high energy electron, 'e' represents a low energy electron, and 'M' is a third collision partner that can be O_2, N_2, etc.

The NO reacts further with O_3 or its precursor O through reactions such as the following [20,21]:

$$O_3 + NO \rightarrow O_2 + NO_2, \quad (5)$$

$$O + NO + M \rightarrow NO_2 + M, \quad (6)$$

Since reactions (5) and (6) are fast [20,21], almost all of the NO ends up as NO_2 at room temperature. For example, 1020 ppm O_3, 115 ppm NO_2 and only 0.213 ppm NO in a dielectric barrier discharge [5] and 160 ppm O_3, 200 ppm NO_2 with NO below detection limits in a sliding discharge [23], support the above statement.

The NO_2 may be oxidized further to higher nitrogen oxides through reactions such as the following:

$$O_3 + NO_2 \rightarrow NO_3 + O_2, \quad (7)$$

However, reaction (7) is significantly slower than reaction (5) [20]. Therefore, major products under room temperature conditions remain NO_2 and O_3.

Ozone may be decomposed by the following reactions [20]:

$$O_3 \rightarrow O_2 + O, \quad (8)$$

$$O + O_3 \rightarrow 2O_2, \quad (9)$$

Rates of these reactions are dependent on temperature. The dependence of reaction (8) on temperature is especially strong, increasing with the increase in temperature. Further, the following reaction which is strongly increasing with an increase in temperature [21], becomes dominant at higher temperatures:

$$O + NO_2 \rightarrow NO + O_2 \quad (10)$$

Therefore, most of the NO generators reported so far are based on arc or spark discharges where the gas temperature in the arc or spark is very high – several thousand degrees. Such a high temperature destroys O_3 and minimizes NO-to-NO_2 conversion. For example, a NO generator based on a dc arc (called Plazon) [6,8,9], a pulsed dc arc between rod-to-rod electrodes [15–18], a pulsed dc arc between needle-to-plate electrodes [19] and spark discharge between pin-to-hole electrodes [12–14] have been reported. The arc or spark discharges generated NO as a major product, but small amounts of ozone and NO_2 were still observed. For example, 400–500 ppm NO along with 70–90 ppm NO_2 in the case of dc arc [9] and 455 ppm NO with 138 ppm NO_2 in the case of pulsed dc arc [16] were reported. A microwave discharge-based device was also reported producing up to 2750 ppm NO, but again, with a significant concentration of ozone, i.e., up to 400 ppm [10,11]. Although the temperature in the arc or spark is very high, the hot temperature zone is confined to a very small volume. Therefore, the residence time of the gas in the high temperature zone does not appear to be sufficient for complete destruction of ozone.

We have reported a large area, nonthermal plasma device for bacterial load reduction from wounds and hospital surfaces [23]. It is based on a high current version of a nanosecond sliding discharge along a dielectric surface [24] that is inherently associated with high throughput for chemical reactions [25]. The nonthermal plasma which is generated has a gas temperature which is very low compared to its electron temperature [26]. Since it has been used for treatment of wounds without causing burns, it is assumed that the gas temperature is close to room temperature. This device was found to be scalable either by increasing the effective length of the electrodes or by stacking and operating multiple discharge chambers in parallel [27]. The electric field distribution in the device assures strong attachment of the discharge plasma to the dielectric surface [28]. It therefore allows controlling plasma chemical reactions through surface mediation. For example, adsorption of O on the dielectric surface in contact with the plasma followed by formation of O_3 or NO may occur [29,30]:

$$O_{ad} + O_2 \rightarrow O_{3ad} \rightarrow O_3, \quad (11)$$

$$O_{ad} + N \rightarrow NO, \quad (12)$$

where 'ad' represents the adsorbed state of the specie.

In this study the effect of temperature on NO production and on byproduct NO_2 and O_3 are explored. The hypothesis is that if the dielectric surface in contact with the plasma is heated to several hundred degrees above room temperature, it can destroy the ozone at the point of its formation on the surface. Heating of the entire discharge chamber, which includes heating of the dielectric surface, can potentially destroy ozone formed in the gas as well. These processes can minimize the conversion of NO into NO_2. A small amount of NO_2 may be formed, e.g., through reaction (6). A fraction of the NO_2 produced at a relatively high temperature may be converted back to NO (via reaction (10)) leaving behind less NO_2 and more NO in the product. This study revealed that heating the dielectric surface to a few hundred degrees above room temperature not only eliminated ozone and minimized nitrogen dioxide, but resulted in a significant increase in the concentration and energy yield for the nitric oxide product. The science behind these useful results regarding nitric oxide production is explained.

2. Experimental

The schematic of the experimental setup is shown in Fig. 1. The plasma reactor was a modified version of the one used earlier for fuel reforming [31]. The reactor comprised: (i) a stainless steel box having an interior cavity with dimensions of 232 mm × 73 mm × 16 mm, with gas inlet/outlet ports and a port for the high voltage lead; (ii) Macor sheets of 232 mm × 73 mm × 2.4 mm as the dielectric layers; (iii) spacers made of 73 mm × 29 mm × 11 mm Macor with multiple holes or slits for holding electrodes and for gas communication; (iv) cathodes that were the exterior of the stainless steel box and two stainless steel rectangles of 127 mm × 11 mm × 3.2 mm separating the inside cavity into three chambers; and (v) six anodes made of stainless steel wire 150 μm diameter and 127 mm effective length each, three placed on the top dielectric layer and the other three on the bottom dielectric layer, as shown in Fig. 2. The distance between the high voltage wire anode and the cathode plates directly exposed to it was 11.1 mm while the distance between the wire anode and shield/cathode on the opposite side of the dielectric layer was 2.4 mm. The total surface between the electrodes, which corresponds to the area covered by the plasma, is therefore ~169 cm^2.

The power lead connected to the high voltage wire anode was insulated from the outer stainless steel box using a flexible insulation tube that is stable at high temperatures up to 450 °C. The reactor was designed to withstand high temperatures up to 450 °C, but the temperature did not exceed 420 °C in this study. The reactor was wrapped with heating tape and a ceramic fabric pad/cloth