

DETERMINATION OF OH RADICAL CONCENTRATION IN DIELECTRIC BARRIER DISCHARGES BY CO OXIDATION

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Abstract: OH radicals play an essential role in various plasma-chemical processes aimed at removal of volatile organic compounds (VOC), NO_x and SO₂ from polluted off-air flows. For the optimization of OH radical generation in non-thermal plasma discharges a simple but reliable diagnostic method is useful and necessary. We report about the oxidation of carbon monoxide as a diagnostic tool for OH radical determination in dielectric barrier discharges (DBD) at atmospheric pressure. The results are discussed in terms of a simple kinetic model allowing the determination of the average OH production efficiency (G_{OH}-value) and the OH lifetime in dependence on air flow humidity.

1. INTRODUCTION

Non-thermal plasmas are hopeful tools to treat pollution of low concentration in atmospheric gases. Such plasmas are generally produced by e-beams, DBD or corona discharges. For the oxidation of VOCs in off-air streams oxidising agents have to be produced by collisions of energetic electrons with matrix gas molecules like O₂ and H₂O.

OH radicals are one of the most important oxidising agents necessary for example for the plasma treatment of aromates and acetates in air. In discharges they are mainly generated by dissociation of water molecules by direct electron and excited atomic oxygen (O(¹D)) impact. At atmospheric pressure their lifetime is very low, usually in the order of some 100 μs.

OH radicals in ac or pulsed discharges have been measured by laser-induced fluorescence (LIF) [1,2] and resonant absorption spectroscopy [3]. In [4] ¹⁴CO is used as a tracer for measurement of atmospheric hydroxyl radical concentrations. Su et al. [5] have applied the non-radioactive version of this method to a non-thermal argon-water plasma. In this paper we present results on OH radical concentration measurements in the humid air plasma of a DBD.

2. EXPERIMENTAL SET-UP

The laboratory scale DBD reactor consisted of a cylindrical glass barrier of 400 mm length with an inner diameter of 23 mm. An outer metallic mesh served as ground electrode and a stainless steel tube of 21.3 mm diameter as hv electrode leaving a gap of approximately 1 mm. The reactor was excited by positive pulses of 19 kV amplitude, 45 μs rise time and a pulse repetition rate of 1-107 pps.

The pulse energy was determined using the voltage-charge method. The discharge voltage and the voltage at the integrating capacitor were recorded by hv probes and a digital storage oscilloscope. The area of the Lissajous figure, representing the energy deposited during one period, was typically 50-60 mJ. At maximum repetition rate around 90 Wh/Nm³ of plasma power per unit volume flow could be applied.

Gas flows of 1 and 2 NI/min (STP) were prepared by means of mass flow controllers from zero air

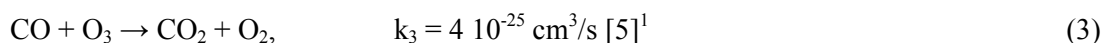
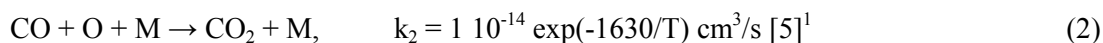
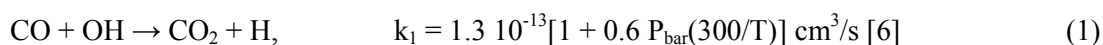
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(21 % O₂ in N₂). Given the plasma volume of 23.7 cm³ a gas flow of 1 NI/min corresponds to a residence time of 1.4 s. The main part of the flow (typically 90 %) was humidified by bubbling it through distilled water of 20-22 °C and a cooling trap at 19 °C resulting in ~2 % of water vapor. The less part (typically 10 %) was mixed with carbon monoxide and added to the main flow upstream to the plasma reactor.

CO and CO₂ concentrations were measured by means of a calibrated NDIR absorption detector downstream to the plasma reactor. Because of cross interference from synthesised ozone carbon monoxide could be measured only in case of no discharge. So for the oxidative removal of CO it was necessary to follow the changes of CO₂ concentration. During several hours the stability of the CO₂ sensor was better than 1 ppm.

3. EXPERIMENTAL RESULTS

In a discharge plasma in humid air at temperature T and pressure P carbon monoxide can be oxidised in several ways:



Furthermore carbon dioxide can be dissociated by direct electron impact:



It was confirmed experimentally that our DBD plasma with low energy density through reactions (2-5) does not influence neither the CO nor the CO₂ concentration in the ppm range. So carbon monoxide removal during plasma treatment is strongly related to the appearance of carbon dioxide: $\Delta\text{CO} = \Delta\text{CO}_2$.

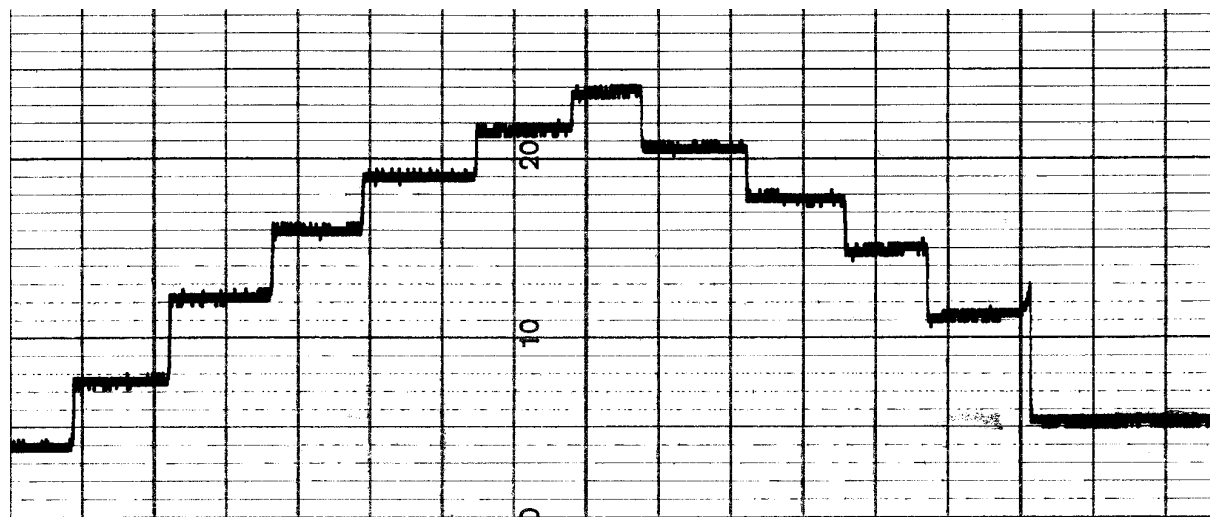


FIGURE 1. CO₂ concentration versus time (from right to left) during oxidation of 51 ppm CO in 1 NI/min humid synthetic air (~2 % of water vapour) at different energy densities, vertically: 0,7 ppm CO₂/unit, horizontally: 10 min/unit

Humid air flows containing 51, 153, 255, 510, 765 and 1020 ppm CO were treated by non-thermal plasma in dependence on energy density E. Fig. 1 shows an example of a CO₂ concentration trace

¹ NIST database

versus time. The steps represent increasing and decreasing energy densities of the DBD. The initial and final CO₂ concentrations differ by 0,9 ppm. The corresponding removal rates R are shown in Fig. 2. The solid lines represent exponential fits from which, according to the relation

$$R = 1 - [\text{CO}(E)]/[\text{CO}(0)] = \exp(-E/\beta) \quad (6)$$

the β -parameter [7] for CO oxidation can be deduced. As it is suggested by Fig. 3, the β -parameter is a linear function of initial concentration CO(0). Its absolute values range from 300 to 600 Wh/Nm³.

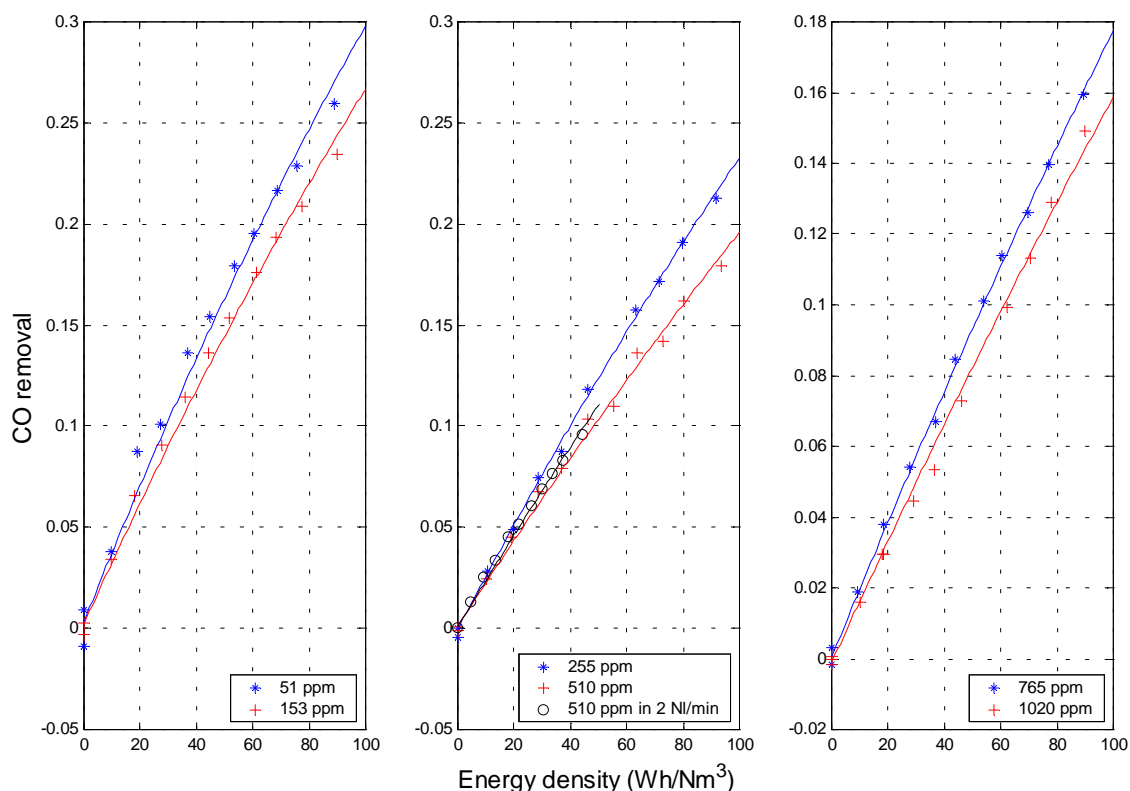
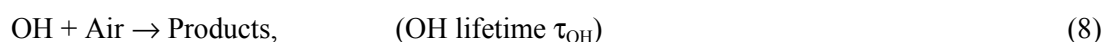


FIGURE 2. Oxidative removal of carbon monoxide in 1 NL/min humid synthetic air (~2 % of water vapour) in dependence on plasma energy density

4. KINETIC MODEL FOR CO OXIDATION

Assuming that oxidative removal of CO in humid synthetic air is based on Eq. (1), the experimental results can be described by a simple model, which in addition to Eq. (1) takes into account OH formation by plasma as well as OH scavenging by “air” molecules:



The corresponding rate equations for CO and OH are

$$d[\text{CO}]/dt = -k_1 [\text{CO}] [\text{OH}], \quad d[\text{OH}]/dt = Q(E) - [\text{OH}]/\tau_{\text{OH}} - k_1 [\text{CO}] [\text{OH}] \quad (9)$$

where Q is the radical source term ($Q = G_{\text{OH}} E/\tau$), G_{OH} is the average radical production efficiency (G-value), τ is the residence time and t is time ($t = x/v$, x – reactor coordinate, v – flow velocity).

In the case of low CO removal ($R \ll 1$) and short living OH radicals ($\tau_{\text{OH}} \ll \tau$) these equations can be solved analytically

$$[\text{CO}(E)] = [\text{CO}(0)] \exp(-E/\beta), \quad \beta = (k_1 \tau_{\text{OH}} G_{\text{OH}})^{-1} + [\text{CO}(0)] G_{\text{OH}}^{-1} \quad (10)$$

In agreement with experimental results β is a linear function of initial CO concentration. The slope of this function is inversely proportional to G_{OH} . Fitting the straight line of Fig. 3 to this relationship a G-value of 3,4 ppm/(Wh/Nm³) and an OH radical lifetime of 200 μ s are obtained. These values are in the same range as reported by Hilbert et al. [3] from resonant absorption spectroscopy studies. According to Eq. 10 they correspond to an average OH concentration

$$[OH] = Q(E) \tau_{OH} = G_{OH} E \tau_{OH}/\tau \quad (11)$$

of approximately $4.9 \cdot 10^{-4} E$ ppm/(Wh/Nm³).

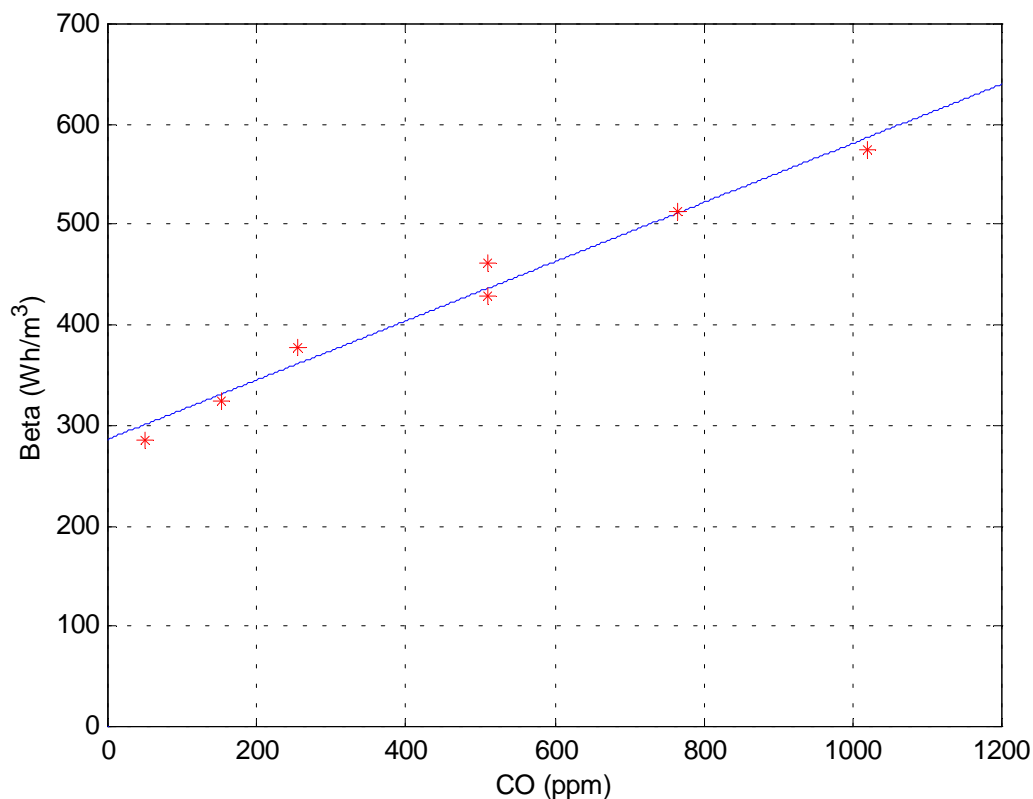


FIGURE 3. β -parameter versus initial CO concentration

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