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# Chemical activity of coplanar DBD with Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> electrodes tested on VOC decomposition

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The chemical effects of coplanar surface DBD at atmospheric pressure in air and air with diluted toluene (300-2500 ppm) were investigated comparing two electrode ceramics – pure Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> coated Al<sub>2</sub>O<sub>3</sub>. In air, the discharge produced mostly ozone, the most effectively for 1000-2000 J/l with TiO<sub>2</sub> ceramic. In air with toluene, the toluene decomposition was observed with the efficiencies increasing with the energy density up to some 2000 J/l, and reaching 50% (Al<sub>2</sub>O<sub>3</sub>) and 70% (TiO<sub>2</sub>). Toluene was decomposed mostly to water, CO<sub>2</sub>, CO and HCOOH. TiO<sub>2</sub> ceramic improved the decomposition efficiency and CO<sub>2</sub> selectivity, and reduced the energy costs and the production of noxious gases, especially NO<sub>2</sub>. Solid organic polymer was deposited on the ceramics but the discharge on TiO<sub>2</sub> ceramic demonstrated a self-cleaning effect.

## 1. Introduction

Diffuse coplanar surface dielectric barrier discharge (DCSBD) is a special arrangement of a DBD where the electrodes are incorporated inside the dielectric material and the discharge is generated on its surface [1]. This discharge can be operated in all gases at atmospheric pressure and generates very homogeneous layer of non-thermal plasma, convenient for a variety of surface treatment applications, such as textile, wood, rubber or glass hydrophilization, etc. [2]. The effect of surface modifications is attributed mainly to reactive species generated in the DCSBD plasma.

The objective of this paper is to investigate the chemical effects of the DCSBD plasma in ambient air and air polluted by VOC (toluene). The VOC abatement application of DBD plasmas have been extensively investigated by many authors during the past decades but coplanar DBD was not tested yet.

## 2. Experiment

### 2.1. Coplanar surface DBD

A simplified arrangement of the DCSBD was used – two silver electrodes in the shape of concentric circles with the mutual distance of 1.5 mm were screen printed on one side of the alumina (96% Al<sub>2</sub>O<sub>3</sub> and 96% Al<sub>2</sub>O<sub>3</sub> coated by sol-gel method with TiO<sub>2</sub> photocatalytic layer) ceramic plate (100x100x1 mm). Silver electrode side was consequently immersed in high voltage insulating oil. The electrodes were energized by 10 kV, 45 kHz harmonic power supplied by LIFETECH VF300.2 power generator. The high voltages were measured by the probes Tektronix P6015A and the current by the Pearson current monitor Model 4100, both

processed by a digitizing oscilloscope Tektronix TDS 2024 (200 MHz, 2.5 GS/s).

The discharge, shown in Figure 1, was generated above the silver electrodes on the surface of the other side of the ceramics. The typical voltage and current waveforms of DCSBS were shown in [2]. The total electrical power output from the network was measured by the power meter. The discharge power was calculated from the voltage and current waveforms using Tektronix Wavestar software.

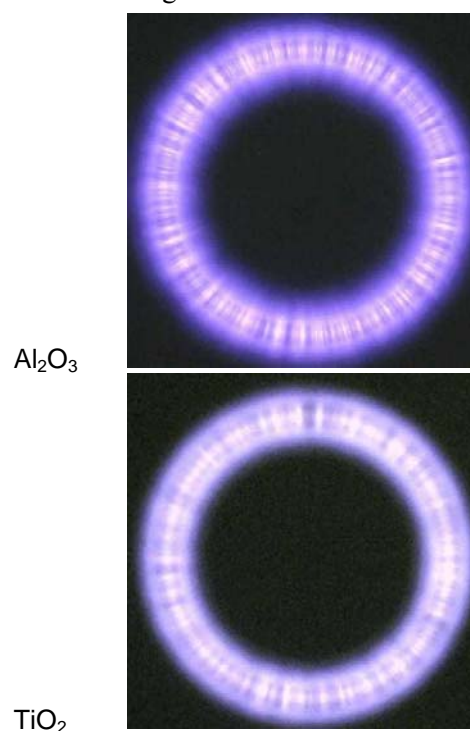


Figure 1. Photographs of the DCSBD (53 kHz, ~35 W) generated on Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> ceramics, 1/10 s exposure.

## 2.2. Gas flow system and diagnostics

The chemical effects of the DCSBD were tested on the decomposition of a model VOC (toluene). The synthetic air as a carrier gas was enriched with toluene vapors in the bubbler with liquid toluene, thus obtaining the saturated vapor pressure at the controlled room temperature, then diluted with pure air in the mixing chamber and lead to the discharge chamber. Two air flow controllers with maximum ranges of 5 (or 1) and 0.25 l/min, respectively, were used to set the total gas flow rate (0.5-5 slpm (standard liter per minute)) and toluene concentration (300-2500 ppm). The gas flow system was practically the same as the one used in our previous work [3].

Despite the discharge chamber volume (ca 25 cm<sup>3</sup>) was not optimized to the plasma volume, it was simply used to test the DCSBD chemical effects. The residence time of the gas in the chamber was 1.5 s at the typical flow rate of 1 slpm.

Fourier transform infrared (FTIR) absorption spectroscopy was used as diagnostics of the untreated and treated toluene-rich air samples using Bruker Vector 22 spectrometer with 1 cm<sup>-1</sup> resolution and spectral range 4000–600 cm<sup>-1</sup>. A glass gas cell with 10 cm length and CaF<sub>2</sub> or KBr windows was used. The gas samples were taken by an iso-kinetic sampling before and after the discharge into the plastic sampling bags and immediately transported to the spectrometer.

## 3. Results and discussion

### 3.1. Chemical effects of DCSBD in air

The discharge power was slightly lower with TiO<sub>2</sub> coated ceramic (32 W) compared to Al<sub>2</sub>O<sub>3</sub> (35 W). The TiO<sub>2</sub> surface exhibited higher breakdown voltage by (0.9±0.2) kV<sub>p-p</sub> and higher probability for the microdischarge to reappear at the same spot.

The chemical effects of the DCSBD in pure synthetic air were demonstrated on the FTIR spectra (Figure 2). The discharge in air produced mainly ozone, then N<sub>2</sub>O and HNO<sub>3</sub>. KNO<sub>3</sub> was an unavoidable deposit forming on KBr windows of the gas cell due to reaction with N<sub>2</sub>O and HNO<sub>3</sub>.

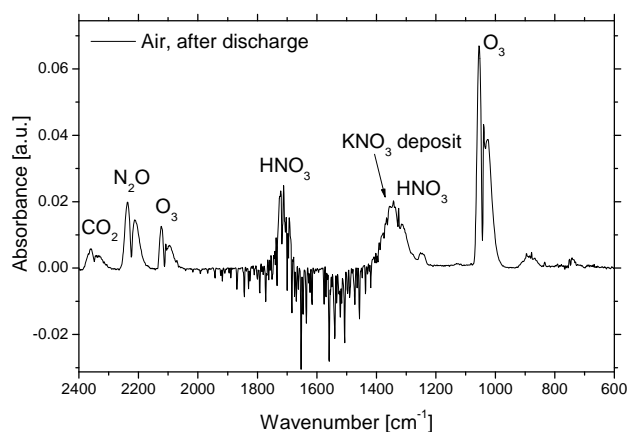


Figure 2. Typical FTIR spectrum of air after discharge treatment at 1 slpm, TiO<sub>2</sub> ceramic.

The production of ozone (measured as absorbance of the spectral band 1055 cm<sup>-1</sup>) as a function of energy density (specific energy input, i.e. power divided by the gas flow rate) is shown in Figure 3, demonstrating the maximum at 1000-2000 J/l. At high energy densities, too much gas heating quenched the ozone production. TiO<sub>2</sub> ceramic produced more ozone than pure Al<sub>2</sub>O<sub>3</sub>.

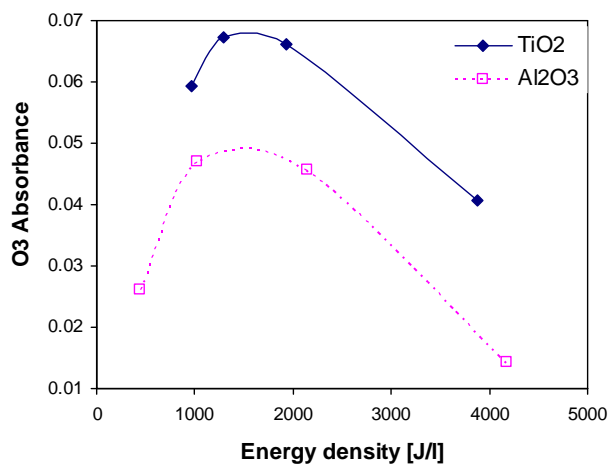


Figure 3. Ozone production by DCSBD in air as a function of energy density, based on 1055 cm<sup>-1</sup> absorption band.

### 3.2. Decomposition of toluene

The typical spectra of 1000 ppm toluene in air before and after discharge are shown in Figure 4. The decomposition of toluene was measured from the decrease of the absorbance of the typical toluene absorption bands at 729 and 3040 cm<sup>-1</sup>.

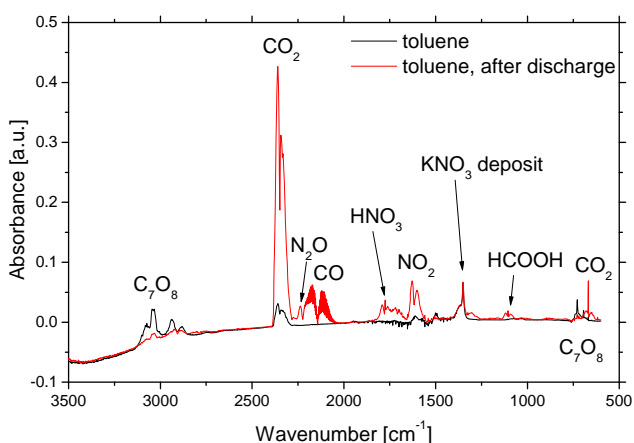


Figure 4. Typical spectrum of 1000 ppm toluene in air (1 slpm) before and after discharge, TiO<sub>2</sub> ceramic

The toluene decomposition process can be characterized by the removal efficiency and the energy costs (energy per one destroyed molecule of toluene). The efficiency did not change too much with the initial toluene concentration. Both parameters as functions of the energy density are shown in Figure 5 and 6, comparing the two ceramics. The TiO<sub>2</sub> ceramic seems better for both higher efficiency and lower energy costs. The removal efficiency exhibited a maximum at about 2000 J/l that corresponds to the air flow rate of 1 slpm. Lowering the flow rate resulted in excessive reactor heating and subsequent efficiency decrease. Further improvement of the performance of the toluene decomposition process can only be achieved by optimizing the reactor – reducing its total volume with respect to the discharge volume.

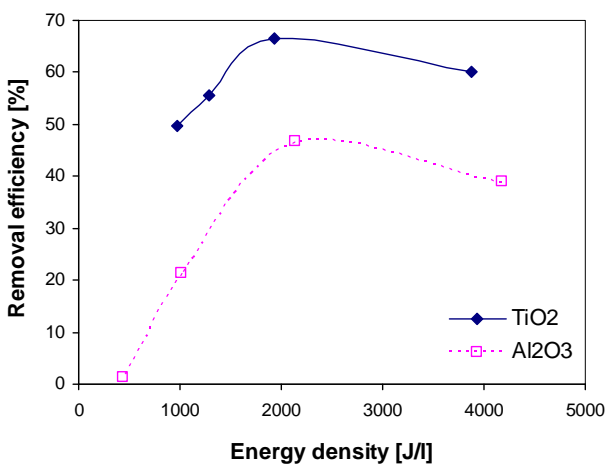


Figure 5. Toluene (1000 ppm) removal efficiency as a function of energy density, based on 3040 cm<sup>-1</sup> absorption band.

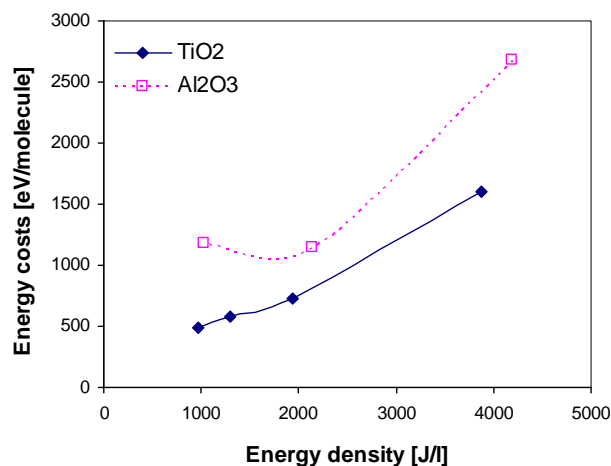


Figure 6. Energy costs for toluene (1000 ppm) removal as a function of energy density, based on 3040 cm<sup>-1</sup> absorption band.

### 3.3. Products of the toluene decomposition

The main gaseous products from toluene decomposition were CO<sub>2</sub>, CO and HCOOH and H<sub>2</sub>O. Their concentration (determined as absorbance of the FTIR spectral bands of 2360, 2172 and 1105 cm<sup>-1</sup>) first increased with the energy density, reached maximum and then decreased, as shown in Figure 7. This decrease is associated with the decreasing removal efficiency at high energy densities (Figure 5). The production of C-products increased with the increasing initial toluene concentration. The CO<sub>2</sub> selectivity and CO<sub>2</sub>/CO ratio was higher for TiO<sub>2</sub> ceramic, which is favorable since CO is a toxic gas.

The production of ozone by DCSBD in toluene-air mixtures depended on the energy density similar to pure air (Figure 3). It also strongly decreased with the initial toluene concentration, reaching 0 at about 1200 ppm toluene. This indicates that O radicals, responsible for ozone formation, are directly involved in the process of toluene decomposition.

Other undesired gaseous by-products of the process were N<sub>2</sub>O, NO<sub>2</sub> and HNO<sub>3</sub> (spectral bands of 2236, 1630, and 1718 and 1325 cm<sup>-1</sup>). Their production did not depend on the initial toluene concentration; they were produced even in the discharge in air; and increased with the energy density. TiO<sub>2</sub> ceramic lead to the higher production of N<sub>2</sub>O, whereas Al<sub>2</sub>O<sub>3</sub> resulted in the higher NO<sub>2</sub>. Since NO<sub>2</sub> is more toxic than N<sub>2</sub>O, TiO<sub>2</sub> ceramic thus seems better from the viewpoint of noxious by-products.

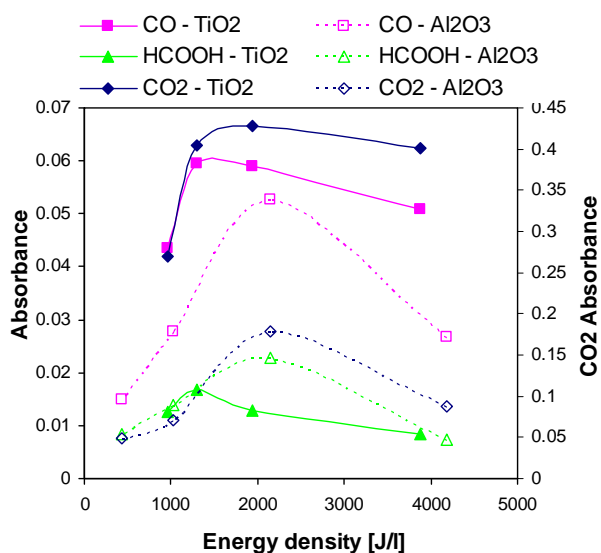


Figure 7. Carbon-containing gaseous products as a function of energy density for both ceramics.

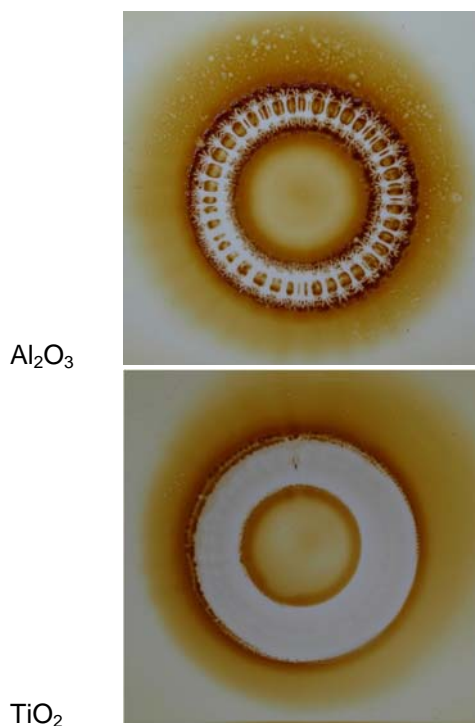


Figure 8. Photographs of the solid deposit formed on the ceramics after toluene decomposition in DCSBD

Besides gaseous products, we observed a brown-yellow solid deposit forming on the ceramics. The preliminary surface ATR (attenuated total reflectance) FTIR analysis indicated it was an organic polymer mixture. A similar deposit was formed when removing toluene in air in a high pressure glow discharge [3]. The electrodes covered with the deposit after several hours of discharge operation are shown in Figure 8. It is very interesting to note that there was no deposit in the

discharge area on TiO<sub>2</sub> coated alumina, whereas Al<sub>2</sub>O<sub>3</sub> was covered even between the microdischarge channels. This is important for practical applications: the DCSBD on TiO<sub>2</sub> ceramics has a self-cleaning effect, in addition to higher efficiency, lower energy costs, higher ozone production, better CO<sub>2</sub>/CO ratio, and lower NO<sub>2</sub> production.

#### 4. Summary

We investigated the chemical effects of coplanar surface DBD at atmospheric pressure in air and air with diluted toluene (300-2500 ppm), comparing two electrode ceramics: pure Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> coated Al<sub>2</sub>O<sub>3</sub>. The discharge chemical effects depended primarily on the energy density. In air, the discharge produced mostly ozone, the most effectively for 1000-2000 J/l with TiO<sub>2</sub> ceramic. In air with toluene, the toluene was decomposed, with the efficiency increasing with the energy density up to some 2000 J/l, reaching 50% with Al<sub>2</sub>O<sub>3</sub> and 70% with TiO<sub>2</sub> ceramics. The corresponding energy costs were high: 1000-2500 and 500-1500 eV/molecule for Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> ceramics, respectively.

Toluene was converted mostly to C-containing gases, such as CO<sub>2</sub>, CO and HCOOH, and water. TiO<sub>2</sub> ceramic improved the CO<sub>2</sub> selectivity and CO<sub>2</sub>/CO ratio. This ceramic also slightly reduced the production of noxious N-containing gases, especially NO<sub>2</sub>. Solid organic polymer mixture was deposited on the ceramics but the discharge on TiO<sub>2</sub> ceramic demonstrated a self-cleaning effect.

The achieved VOC removal efficiencies and energy costs cannot compete with other conventional and plasma sources for VOC abatement. Optimization of the reactor volume and other parameters will be required for further implementation of this discharge type for applications. However, the chemical effects of DCSBD on toluene decomposition and multiple positive effects of TiO<sub>2</sub> coated ceramic electrode were clearly demonstrated.

#### 5. References

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