Ozone generation by surface dielectric barrier discharge with TiO$_2$ photocatalyst

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Applications of ozone have attracted increasing attention from industrial, medical, biological and many other fields. Among the various methods of ozone synthesis, the dielectric barrier discharge plays the most important role. The objective of our work was to investigate experimentally ozone production of the surface dielectric barrier discharge in synthetic air without and with titanium dioxide TiO$_2$ photocatalyst in the discharge chamber. We found that addition of TiO$_2$ into the discharge chamber not only increases concentration of ozone produced by the discharge, but for small values of discharge power almost two times increases ozone production yield. The experiments were performed for the frequency of the driving voltage 11 kHz and mass of the TiO$_2$ globules 3.8493 g.

1. Introduction
Due to its biocide properties ozone becomes interesting for applications like sterilization, water and effluents treatment, food storage etc. The industrial generation of ozone is carried out by electrical discharges breaking down the oxygen molecule, and triggering subsequent processes leading to ozone generation. The most frequently used type of these discharges is dielectric barrier discharge. In spite of the existing state of art the attention of researchers is oriented toward the further improvement of the existing devices. There are numerous ways to enhance discharge ozone production e.g. by combining the discharge with catalysts [1,2], ferroelectrics [3-5], by application of ultrasound [6] or magnetic field [7]. However from the analysis presented in [8] it seems that the most attractive way to increase the performance of the discharge from the standpoint of ozone production is combination of the discharge with a catalyst. There exist different catalysts, which can be used for enhancement of discharge ozone production such as SrTiO$_3$, TiO$_2$, ZnO, ZnS or CdS. The titanium dioxide suites the best the requirements, because it can be activated by the ultraviolet emission from the discharge, is chemically inert, stable and it has well known properties.

The objective of our work therefore was to investigate experimentally the effect of placement of TiO$_2$ photocatalyst on ozone production and ozone production yield of the surface dielectric barrier discharge (SDBD) in synthetic air. The TiO$_2$ cylindrical globules were placed opposite to the high voltage electrode, that is they were exposed to the discharge.

2. Experimental arrangement
The experimental set-up, based on the surface dielectric barrier discharge is shown in Fig. 1. It consists from a discharge ozone reactor, an electric supply unit, electrical parameters diagnostics, an air supply unit and an ozone monitoring system.

![Fig. 1. Experimental arrangement](image-url)
The grounded electrode has a form of a square of dimensions $36.5 \times 36.5$ mm. The layout of the high voltage strip electrode and grounded electrode is shown in Fig. 2.

![Fig.2. Layout of the high voltage strip electrode and grounded electrode.](image)

The alumina plate separates the ozone reactor volume in two parts. The lower part, exposed to the high voltage strip electrode, in which the discharge is generated, is flushed by an air from a cylinder. This air is delivered through the moisture trap and through the mass flow controller (MFC). We also monitored relative humidity of this air (sensor RH) at the input of the discharge volume. A flowing air from the compressor cools the upper part of the discharge chamber, exposed to the ground electrode. At the output of the ozone reactor discharge volume is placed the sensor of temperature (T).

The concentration of ozone at the output of the ozone reactor is measured by the absorption of the 254 nm ultraviolet spectral line with API 450 ozone monitor (range 0-4000 ppm).

The electrical parameters diagnostics consisted in measurement of the average power delivered to the discharge. The power $P$ depends on the discharge voltage $U$ and on the discharge current $i$, that is

$$P(t) = U(t) \times i(t)$$ (1)

As far as both these quantities are functions of time the simultaneous measurements of the discharge voltage and current is required to determine the discharge power.

The discharge voltage $U(t)$ signal was sampled and recorded on the first channel of the digital oscilloscope ADS 1102CM (150MHz) through the high voltage probe HVP-28HF (division ratio 1000/1, frequency up to 200 MHz).

For measurement of current $i(t)$ we used a measuring capacitor $C_{meas} = 0.01 \ \mu F$, connected in series with the grounded electrode of the discharge (see Fig.1). Thus the voltage drop on this measuring capacitor yields the discharge current using the following relation:

$$i(t) = \frac{dq}{dt} = C_{meas} \frac{dU_{cap}}{dt}$$ (2)

The average power was then calculated from integration of instantaneous power divided by corresponding time period.

In order to study the effect of titanium dioxide TiO$_2$ on SDBD ozone generation we placed one layer of Aerolyst 7706 TiO$_2$ globules in the lower part discharge chamber as shown in Fig. 1. The anatase content of this photocatalyst is minimum 70 %, the density is $\sim 3.8$ g/cm$^3$ and the surface area is 40-50 m$^2$/g. The cylindrical globules had the diameter $\sim 3$ mm and the height $\sim 4$ mm.

3. Experimental results

The experiments were performed with the constant airflow of 1.8 slm through the lower part of the discharge chamber, and flow of the cooling air 59 slm through the upper part of the discharge chamber. Relative humidity of the synthetic air was 0.7%. The mass of TiO$_2$ globules placed on the lower wall of the discharge chamber was 3.8493 g.

The results of discharge ozone generation are presented as a function of ozone concentration and ozone production yield versus average discharge power. The ozone production yield $\alpha$, is calculated in the following way:

$$\alpha = \frac{21.4 \times (\text{Ozone conc.}) \times \text{Airflow} \times 6 \times 10^{-3}}{P_{av}}$$ (3)

where ozone concentration is substituted in ppm, airflow in slm, average power in W and ozone production yield is obtained in g/kWh.

For illustrative purposes is in Fig. 3 shown typical waveforms of the discharge voltage and current calculated from Eq. 2.

![Fig. 3. Typical waveforms of the discharge voltage and current. $Q_{\text{disch}}=1.8$ slm, $Q_{\text{cool}}=59$ slm, $f=11$ kHz, discharge without TiO$_2$.](image)
The dependences of ozone concentration versus average power for the discharge without TiO$_2$ and with TiO$_2$ are shown in following Fig. 4. From this figure it is seen that the dependences of ozone concentration versus average power for the discharge with or without TiO$_2$ follow the same trends.

Fig. 4. Ozone concentration versus average power for the discharge without TiO$_2$ and with TiO$_2$. $Q_{\text{disch}}=1.8$ slm, $Q_{\text{cool}}=59$ slm, $f=11$ kHz, $m_{\text{TiO}_2}=3.8493$ g.

The ozone concentration with increasing average power increases, reaches certain maximum and then starts to decrease. Placing the TiO$_2$ into the discharge volume of the ozone reactor for the whole range of investigated average power increases concentration of ozone produced by the discharge. The difference between ozone concentration with or without TiO$_2$ increases with increasing average power. For the highest values of the average power ozone concentration decreases; for the discharge without TiO$_2$ it falls to zero. This decrease of ozone concentration is caused by the discharge poisoning effect [10].

It is seen that ozone production yield decreases with increasing average power and the highest values of ozone production yield are obtained for small values of the average discharge power. Apart of it, it is also seen that addition of TiO$_2$ increases within a whole range of investigated power the ozone production yield. Maximum increase of ozone production yield, almost two times, is obtained for small values of average power.

The obtained results dealing with the effect of TiO$_2$ on discharge ozone production can be understood taking into account contribution of TiO$_2$ activation to the processes leading to the ozone production. The TiO$_2$ is the $n$-type semiconductor with the width of the forbidden gap 3.2 eV, which corresponds to the wavelength of radiation 388 nm. The SDBD in air is a source of ultraviolet radiation. The strongest emissions originate from the second positive system of nitrogen ($C_2\Pi_u \rightarrow B_2\Pi_g$), which emits photons of wavelength 337.1 nm. The first negative system ($B_2\Sigma^+_u \rightarrow X_2\Sigma^+_g$) of N $^+$ emits radiation of the wavelength 391.4 nm. This UV radiation can contribute to photo-excitation of the TiO$_2$, with the subsequent reduction reactions leading to the creation of the negative oxygen ions, and in this way to the enhancement of ozone production processes.

Apart of the UV activation certain role of TiO$_2$ activation can also be played by the generation of new reactive species on the catalyst surface and their contribution to the ozone production processes.

4. Conclusions

We have investigated ozone production of the surface dielectric barrier discharge in synthetic air with presence of the titanium dioxide in the discharge chamber. We found that addition of TiO$_2$ into the discharge chamber not only increases concentration of ozone produced by the discharge, but for small values of power almost two times increases ozone production yield. Though absolute values of ozone production yield are not extremely high we consider as an important result that addition of TiO$_2$ in the discharge substantially increases ozone production yield.

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6. References