Czech Technical University in Prague
Faculty of Electrical Engineering

Intensification of ozone generation through multi-criteria optimization of dielectric barrier discharge

by

Ing. Jan Mikeš, Ph.D.

Habilitation Thesis

June 2023

Faculty of Electrical Engineering
Czech Technical University in Prague
Technická 2
166 27 Prague 6
Czech Republic

Acknowledgements

I would like to thank Professor Stanislav Pekárek for his collaboration with me, and his long-lasting support of my work. My thanks also go to other colleagues and members of the Faculty of Electrical Engineering who did not hesitate to help me whenever needed. I especially thank Professor Jaroslav Knápek who offered me position of a researcher at the Faculty of Electrical Engineering at the Czech Technical University and who supported me and helped me open the *Laboratory of Environmental Electrotechnics and Economics*, of which I am currently in charge.

Abstract

This habilitation thesis comprises an annotated collection of articles published in the years 2014-2023, while exploring possibilities of efficient intensification of ozone generators, operating on the principles of dielectric barrier discharges through multi-criteria optimizations focused on the impact of the environment within which they originate. Top-priority accent was laid on optimizing the direction of the flow of feeding gas (air) in an ozone generator in relation to the microdischarges being generated, to the environmental impacts in which they occur, and the introduction of photocatalytic materials to their vicinity.

Keywords: Surface dielectric barrier discharge (SDBD), Ozone (O_3), Ozone generator, Non-thermal plasma, Air flow, Numerical simulations, Photocatalysts

Abstrakt

Habilitacn prace je komentovanym souborem clanku publikovanych v letech 2014-2023 zabyvajcch se moznostmi efektivnho zvysen ucinnosti generatoru ozonu pracujcch na principech dielektrickych barierovych vyboju prostrednictvm vcekriterialnch optimalizac zamerenych na vliv prostred, ve kterem jsou formovany. Prevazny duraz je kladeny na smerovou optimalizaci prouden pracovnho plynu generatoru ozonu vuci vznikajcm mikrovybojum, vlivum prostred, ve kterem jsou generovany, a implementaci fotokatalytickych latek do jejich blzkosti.

Klcova slova: Povrchovy dielektricky barierovy vyboj (SDBD), Ozon (O_3), Generator ozonu, Netermaln plazma, Prouden vzduchu, Numericke simulace, Fotokatalyzatory

Contents

1 Introduction 1
1.1 Motivation . . . 1
1.2 Importance and objectives of studied phenomena . . . 2
1.3 Structure of the habilitation thesis . . . 3

2 Phenomenology of dielectric barrier discharge 5
2.1 Dielectric barrier discharge behaviour . . . 5
2.2 Dielectric barrier discharge features . . . 6
2.2.1 Active electrode geometry . . . 6
2.2.2 Commonly used measuring setup . . . 8
2.2.3 Electrical parameters of dielectric barrier discharge . . . 10
2.3 Representation of the microdischarge channel development based on 3D numerical study . . . 12
2.3.1 Physical description of the SDBD phenomena . . . 13
2.3.2 Formulation of the problems . . . 15
2.3.3 Discretization . . . 17
2.3.4 Reconstruction of E, Vi, Ve . . . 21
2.3.5 Implementation of the numerical scheme . . . 22
2.3.6 Pseudocode of main scheme . . . 22
2.3.7 Numerical results . . . 23
2.4 Comparison of the suitability electrode systems for O_3 and UV generation 24
2.5 Summary . . . 25

3 Non-electrical parameters of the discharge 27
3.1 Temperature e ect on SDBD . . . 27
3.2 Interaction of SDBD with low speed air ow . . . 31
3.2.1 Perpendicular versus parallel air ow with respect to the microdischarges . . . 32
3.3 Practical outcome for cylindrical ozone generators . . . 36

3.4 Summary 43

4 Photocatalytical e ect on ozone generation by SDBD 45
4.1 Most frequently used photocatalyst 46
4.2 Photocatalyst adjustment 47
4.2.1 Stability of photocatalytic activity 50
4.3 Summary 51

5 General conclusions 53
5.1 Conclusion 53
5.2 Future outlooks 54

Bibliography 57

A Author's publications related to the habilitation thesis 65
A.1 3D printing materials for generators of active particles based on electrical discharges 65
A.2 Driving voltage frequency and active electrode setup e ects on ozone and UV generation of dielectric barrier discharge in air 80
A.3 Temperature-and air ow-related e ects of ozone production by surface dielectric barrier discharge in air 90
A.4 E ect of a diamond layer on the active electrode on the ozone generation of the dielectric barrier discharge in air 99
A.5 Experimental and modelling study of the e ect of air ow orientation with respect to strip electrode on ozone production of surface dielectric barrier discharge 111
A.6 A 3D Numerical Study of the Surface Dielectric Barrier Discharge Initial Phase 123
A.7 Air Supply Mode E ects on Ozone Production of Surface Dielectric Barrier Discharge in a Cylindrical Con guration 141
A.8 Surface Dielectric Barrier Discharge in a Cylindrical Con guration { E ect of Air ow Orientation to the Microdischarges 156
A.9 Catalytic and time stability e ects of photocatalysts on ozone production of a surface dielectric barrier discharge in air 175
A.10 E ect of TiO_2 on Various Regions of Active Electrode on Surface Dielectric Barrier Discharge in Air 184
A.11 Comparative study of TiO_2 and ZnO photocatalysts for the enhancement of ozone generation by surface dielectric barrier discharge in air 199
A.12 Patent c. 308 279 { Zpusob generovan ozonu a dalsch aktivnch castic a zarzen k provaden tohoto zpusobu 207

List of Figures

1.1 Electrodes with burning discharge. 2

2.1 2D geometry of the active strip electrode. 7
2.2 2D geometry of the grounded electrode. 7
2.3 Geometry of the cylindrical active electrode - rings. 7
2.4 Geometry of the cylindrical active electrode - strips. 7
2.5 Experimental arrangement. 8
2.6 Particle injector for ow visualisation. 9
2.7 Detail of visualised ow patterns. 10
2.8 Principle of the surface dielectric barrier discharge. 11
2.9 Trajectories and velocities of ions V_i at time 18 ns. 23
2.10 Trajectories and velocities of electrons V_e at time 18 ns. 23
2.11 Luminous region around the strip electrode. 23
2.12 Darker regions between two adjacent strips. 25

3.1 The main reactions leading to ozone generation and depletion. 30
3.2 Symmetrical electrode. 33
3.3 Horizontal cross-section of the symmetrical chamber. 33
3.4 Vertical cross-section of the symmetrical chamber. 33
3.5 Ozone concentration versus discharge power for symmetrical electrode and relevant air ows. 34
3.6 Numerical simulation of the velocity eld in the symmetrical chamber. 34
3.7 Ozone concentration versus e ective discharge voltage for the air ow 2 slm. . . 35
3.8 Ozone concentration versus e ective discharge voltage for the air ow 8 slm. . . 35
3.9 E ective voltage versus discharge power for the air ow 2 slm and 8 slm, respectively. 36
3.10 Phase shift versus e ective discharge voltage for the air ow 2 slm and 8 slm, respectively. 36
3.11 Ozone concentration for the strips active electrode, air inputs 1A and 4A and temperatures 10°C (full symbols) or 20°C (empty symbols). 37

3.12 Ozone concentration for the rings active electrode, air inputs 1A and 4T and temperatures 10°C (full symbols) and 20°C (empty symbols). 37
3.13 Ozone concentration versus instantaneous discharge power for the strips active electrode and one air input nozzle oriented radially (R), axially (A), and tangentially (T). 37
3.14 Ozone concentration versus instantaneous discharge power for the rings active electrode and one air input nozzle oriented radially (R), axially (A), or tangentially (T). 37
3.15 Geometries of the optimized cylindrical active electrode - A-type. 38
3.16 Geometries of the optimized cylindrical active electrode - B-type. 38
3.17 COMSOL Multiphysics streamline simulation for 5 SLM. 39
3.18 Ozone concentration versus instantaneous discharge power for the A-type electrode. 39
3.19 Ozone concentration versus instantaneous discharge power for the B-type electrode. 39
3.20 Ozone production versus air ow for the A-type electrode. 40
3.21 Ozone production versus air ow for the B-type electrode. 40
3.22 Di erence in ozone production between two types of electrode systems (blue area - A-type, red area - B-type). 41
3.23 Ozone generator with optimized air ow patterns with microdischarge orientation. 42
3.24 Proposal of ozone generator prototype. 42

4.1 Basic mechanism of photocatalyst e ect. 46
4.2 The surface dielectric barrier discharge spectrum in air for the wavelengths of 330 to 480 nm. 47
4.3 Ozone concentration versus discharge power for plate with introduced photocatalysts. 48
4.4 Ozone concentration versus discharge power for plate with pyramides and introduced photocatalysts. 48
4.5 Ozone concentration versus discharge power for places with introduced photocatalysts. 49
4.6 Emission spectra of the discharge with various regions of the active electrode covered by TiO_2. 49
4.7 Time dependences of ozone concentrations generated by the discharge without and with photocatalysts. 50
4.8 Phase shifts between applied voltage and current for the discharge without and with various photocatalysts as a function of the e ective voltage. 52

Chapter 1

Introduction

1.1 Motivation

The usage of dielectric barrier discharge (DBD) [1] has been on the rise in many applications, such as active particles, ozone, and ultraviolet (UV) generation [2] (available in Appendix A.1), pollution control [3], surface treatment [4], [5], plasma-chemical vapour deposition [6], in medical, biological and chemical applications (sterilization, deodorization, bacterial deactivation, and prolongation of food storage) [7], and air- ow control [8], [9].

The chemically reactive species, together with UV radiation generated by electrical discharges, are responsible for high nonthermal plasma reactivity, which can be utilized for a variety of above-mentioned applications [10], [11].

From all of the properties of DBD, we have selected generation of ozone as it o ers the strongest oxidizing e ects and can be quanti ed well. UV radiation can be further employed for the inactivation of bacteria and viruses, sterilization, disinfection and surface treatment [12]. UV radiation can also serve for photocatalytic activation [13].

Ozone is produced by DBD or corona discharges (CD) from oxygen or air. Our study prioritizes e cient ozone production and UV radiation of DBD in air. Another method of ozone production is the photochemical method, which makes use of UV radiation. Chemical, thermal or electrochemical methods can be also applied. The individual methods di er in the type of energy needed to dissociate the oxygen bonds during ozone production. In spite of the fact that ozone production from air is accompanied by occurrence of nitrogen oxides, many types of commercial ozonizers use air as a feeding gas, as is the case in this study.

Ozone generation in a DBD in air at atmospheric pressure constitutes a complex process involving a number of ozone generation as well as ozone decomposition reactions [14]{[17]. In a DBD, current ow is brought about by a large number of statistically distributed microdischarges [18]. Since ozone, mainly formed in the microdischarge channels, di uses immediately after its generation into the discharge volume [14], [19], its production is a ected by the number and distribution of microdischarge channels as well as their properties. These properties can be in uenced by the electrical parameters of the discharge, gap spacing, or properties of the dielectric layer and the metal active electrode used (see examples in Fig. 1.1). Consequently, discharge ozone production is a result of a combination of all these factors.

(a) Honeycomb. (b) Strips. (c) Mesh.

Figure 1.1: Electrodes with burning discharge.

1.2 Importance and objectives of studied phenomena

Ozone generation by means of dielectric discharges gures among the most e cient and competent methods of its preparation. However, seen from an economic point of view, it also ranks among the most expensive methods. Viewed against the current trend in society seeking widespread sanitization in its various segments, the stage has now been set for the vital need to produce and introduce a wide scale of devices, ranging from stationary high-capacity generators to mobile as well as hand-held battery-operated generators.

The research results summed up in this habilitation thesis respond to the speci c needs of the commercial sectors, re ecting the current issues pertaining to the energy, materials as well as electronic crisis; this research concentrated on multi-criteria optimization of ozone generation, primarily through optimization of the direction of the ow of feeding gas in relation to microdischarges resulting from DBD.

Even though ozonés indisputable advantage during dissociation is its decomposition into atomic or rather molecular oxygen, the remaining negative aspect is its non-selective oxidation interaction with surrounding surfaces and objects, and concurrent generation of nitrogen oxides. These factors have to be taken into consideration in the actual design and construction of ozone generators.

Proceeding from targeted studies of the issues concerning dielectric barrier discharges based on the preparation of ozone, multi-criteria optimization methods leading to intensi- cation of ozone generation have been proposed. The hitherto frequently neglected factors

{ optimizing the direction of the flow of feeding gas in ozone generator's chamber, adequate provision of environmental conditions on the site of their origin, and introduction of photocatalytic materials to their vicinity { were primarily reflected in this research. The procedures outlined here are conducive not only to enhancing the overall efficiency of ozone generators by as much as dozens of percent, but { at the same time { to providing a vital context for continuing basic research in the physics of nonthermal plasma. The motivations of the results presented in this thesis are therefore both technical (practical) and fundamental.

1.3 Structure of the habilitation thesis

This habilitation thesis is divided into three interconnected thematic units describing { on the basis of long-term investigation of the interactions of DBD with external environment { the possibilities of upgrading the efficiency of ozone generation by means of multi-criteria optimization.

The first part analyzes the general electrical parameters of dielectric discharge in a stationary environment of an immobile feeding gas. Also under scrutiny is the importance of the geometry of the electrode itself, together with the impact on amplitude and frequency of the applied electric voltage, current peaks and phase shifts of currents originating during microdischarges. Our own numerical 3D model simulating behaviour of a dielectric discharge reflecting the geometry of the mutual position of electrode systems has been designed, constructed and tested for the options of multi-criteria optimizations. The results thus gained by the model facilitate their direct implementation in the process of practical design of ozone generators.

Follow-up investigation focused on the impact of the vicinity on the microdischarges being generated, primarily on the effect of ambient temperature and directionally oriented low-speed air flow of feeding gas on the microdischarges occurring during a DBD. These phenomena were studied both in planar and cylindrical configurations of the electrode systems. The chief outcome of this section of my habilitation thesis is a body of findings applicable in the practical designing of ozone generators, with systematic optimization of the flow of feeding gas in relation to the orientation of microdischarges being capable of enhancing their efficiency.

The final, third part of the thesis discusses the importance of introducing photocatalytic substances into the environment of electrical discharges, as seen from a theoretical, experimental as well as practical point of view. UV radiation, which is also generated by SDBD, may be utilized for the activation of photocatalytic materials participating in the generation of other excited particles, and thus increasing the amount of generated ozone. Significance of the following photocatalysts: TiO_2, ZnO, $BaTiO_3$ a WO_3 was examined in particular.

Chapter 2

Phenomenology of dielectric barrier discharge

Dielectric barrier discharge is an electrical discharge created between a minimum of two electrodes, at least one of which is covered by an insulant. The distance between electrodes is typically several millimetres (defined by the thickness of the dielectric material).

By connecting these electrodes to alternating high voltage sources and under the pressure of surrounding feeding gas ranging from 0.01 to 10 MPa will give rise to generation of strong local electric fields and thus surface and spatial separation of the electric charge which may cause the generation of electron avalanches resulting in the origin of microdischarges. Microdischarges with a diameter of 100 µm cover the entire area of the electrodes and last for a period from 1 to 100 ns. During each discharge, an electric charge of the size 10^{2}-10^{3} pC with current density up to 10^{5} A/m^{2} is transferred. This generates a nonthermal plasma showing the characteristics of electron density from approximately 10^{14} cm^{-3} to values higher than 10^{15} cm^{-3}, and with mean electron energies ranging from 1 eV to values higher than 15 eV. Plasma originating under such circumstances is also accompanied by the generation of UV radiation.

2.1 Dielectric barrier discharge behaviour

According to the space in which dielectric discharges are generated (regarding the configuration of electrodes), they can be further classified into the Surface Dielectric Barrier Discharge (SDBD), providing the surface of the active electrode is covered by an additional dielectric layer, the Coplanar Dielectric Barrier Discharge (CDBD), and finally the Volume Dielectric Barrier Discharge (VDBD) types. VDBD has been the most frequently investigated type because it is easier to perform in technical terms. The applied voltage and its frequency, just as the thickness and type of dielectric layer, and the configuration of the electrode motive determine and directly affect the type of discharge that occurs on the surface of the dielectric material.

In my research I have zeroed in on SDBDs, originating on the surface of an active electrode, which was driven by the sinusoidal low-frequency voltage.

2.2 Dielectric barrier discharge features

2.2.1 Active electrode geometry

2.2.1.1 Properties of dielectrics layers

SDBD has been frequently studied within a planar experimental con guration, where one electrode connected to an alternating high-voltage power supply system and serving as a high-voltage (active) electrode is applied to one side of a planar dielectric plate (barrier) by means of screen printing, steaming, and dusting or, eventually, is cut out of a thin foil made of an electrically conductive material (copper, aluminium, stainless steel, special steel) and is glued by conductive glue. An optional procedure could be the use of a thin conductive mesh.

A grounded electrode, often made of the same material in an oblong or square shape and overlapping the active electrode surface by several millimetres, is located on the lower (opposite) side. The actual shape of the active electrode is usually selected in keeping with the purpose to be served by the designed generator of active particles and ozone (it can also be a source of ultraviolet radiation). The con guration frequently features thin parallel strips, circles, and segments shaped as a honeycomb, but it can also take the shape of a mesh (see Fig. 1.1).

In case of my study, dielectric barrier discharge was gradually investigated on several types of con gurations of dielectric systems. The rst two con gurations were planar, made of Alumina, produced by the company Elceram. The Alumina plate contained 96% Al_2O_3, mass density of 3.7 g/cm^3, roughness 0.25-0.7 µm, the dielectric constant for 1 MHz of 9.6, electric strength of 14 kV/mm and heat conductivity for a temperature of 25°C of 24 W/m K. The dimensions of this plate were 50 Ö 50 Ö 0.635 mm, and 110 Ö 110 Ö 0.635 mm, respectively. Both types, laboratory-prepared and also commercially available electrodes used in industrial ozone generators, were tested.

The last assembly was a cylindrical dielectric tube made of Simax glass with an outer diameter of 20 mm and an inner diameter of 17.4 mm, and length of 150 mm. The relative permittivity of Simax glass, at temperature 20°C and frequency 1 MHz, amounted to 4.6.

2.2.1.2 Electrically conductive material of active electrode geometry

In the rst example, the active electrode system was produced by screen printing, using the DuPont nickel-based paste 9538. The sheet resistivity of the layer made from this paste amounted to 30-60 m /sq at 25 µm thickness.

A 0.035 mm thick copper foil, manufactured by the Elchemco company, was used in other cases. The last sample to be used was a 0.025 mm thick aluminium foil from the Anticor company. Both were glued on the Alumina plate or the Simax tube's outer side.

2.2.1.3 The shape of active electrode geometry

An electrode formed by 9 or 14 interconnected strips respectively, 1 mm thick, with a 3 mm distance between one another, was employed for planar configurations. An example of specific geometry used in the articles [20]–[25] published in Appendices A.2, A.3, A.5, A.6, A.10, A.11 is shown in Fig. 2.1 and Fig. 2.2.

Figure 2.1: 2D geometry of the active strip electrode.

Figure 2.2: 2D geometry of the grounded electrode.

The same dimensional geometry (strip thickness 1 mm and a 3 mm distance between neighbouring electrodes) was maintained with cylindrical systems (see Fig. 2.3 and Fig. 2.4) even though the selected shape of electrodes featured interconnected rings, eventually longitudinal or inclined strips.

Figure 2.3: Geometry of the cylindrical active electrode - rings.

Figure 2.4: Geometry of the cylindrical active electrode - strips.

Electrodes made of stainless steel meshes, eventually with a deposition of the following metals: titanium, vanadium, zirconium, molybdenum and copper, were tested for specific purposes. The appropriate choice of dielectric material and electrode material improves the lifetime of the DBD system.

2.2.2 Commonly used measuring setup

The laboratory equipment for the evaluation of physical-engineering parameters was set up by employing an experimental system that allowed for autonomous management of experiments and data collection. The power system comprised a function generator, power amplifier with a transformer, safety features, wiring and devices for the measurement of electric quantities in the shape of voltage and current probes, and a power analyzer.

The pneumatic section of the system was composed of a compressor, equipped with a dehumidifying mechanism, devices for conducting feeding gas, a control valve and components for measuring non-electric quantities, such as gas temperature and humidity in various parts of the system, pressure and concentration of O_3. The experimental setup is depicted in Fig. 2.5.

Figure 2.5: Experimental arrangement.

Two methods were used to keep the temperature of the discharge chamber constant (for reasons see the [21], [26] in Appendices A.3, A.8, and compare with Chapter 3.1). Firstly, the cooling water flowing through the radiator (for example a central brass tube) was supplied to the thermostat WCR P12. The temperature of water T_W was controlled in this way. Secondly, the discharge chamber was placed into the cooled thermo box POL-EKO-APARATURA, offering the possibility of regulating temperature from +3 to +70 °C with an accuracy of $\pm$ 0.1°C. The experiments were performed with the cooling water T_W temperature, and temperature in the thermo box T_T was adjusted as required.

Air is supplied from an oil-free compressor through a membrane dryer (MD) and a system of air filters and a mass flow controller (MFC). The relative humidity RH, temperature T_1, and pressure P of the air prior to discharge chamber input (see Fig. 2.5) were monitored. Also measured was temperature T_2 of the air at the discharge chamber output. An RH sensor was installed to monitor relative humidity. A digital manometer detected the pressure Siemens Sitrans P. Finally, air temperature was measured by the optical fibre thermometer Neoptix. BMT 964 or API 450 ozone analyzers measured the concentration of generated ozone at the discharge chamber output.