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Plasma chemistry in non-equilibrium discharges: discharge physics and applications

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Abstract

Non-equilibrium (cold) plasmas operated at or close to atmospheric pressure have become very important. Recent progress in the operation of corona discharges and dielectric-barrier discharges and their applications is discussed. New large-volume applications include high-power excimer ultraviolet lamps, excimer based fluorescent lamps and large-area flat plasma display panels. Novel processes include the treatment of large gas flows for odour and pollution control and the selective functionalization of flat surfaces, fibres, fabrics and powders. Further innovative applications can be expected from the combination of recently developed microcavity plasma devices, DBD operation and microfabrication technologies suited for mass production. Large arrays of parallel miniature non-equilibrium discharges can be operated simultaneously. If small apertures are used gas can be fed through these microplasmas, thus creating the unique possibility to combine microreactor technology with non-equilibrium plasma chemistry and possibly also catalysis.

Keywords: Corona discharges; Dielectric-barrier discharges; Microplasmas; Microreactors

1 Introduction

The two major representatives of atmospheric-pressure non-equilibrium discharges (cold plasmas) with electron temperatures far in excess of heavy particle temperatures are corona discharges used in electrostatic precipitators and copying machines and dielectric-barrier discharges (DBDs), originally mainly used for large-scale industrial ozone generation. Recent advances in the understanding of the discharge physics and reaction kinetics of atmospheric-pressure non-equilibrium

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discharges and improvements in technology have led to a number of novel applications including high-power excimer ultraviolet lamps, excimer based fluorescent lamps and large-area flat plasma display panels. Additional applications can be found in pollution control devices and in processes used for advanced surface modification. Currently investigated processes include the cleaning, functionalization, sterilization, decontamination and coating of metal and polymer surfaces and the treatment of textile fibres and fabrics [1,2]. Non-equilibrium discharges can initiate an electron driven chemistry or free radical chemistry without much heating of the main gas flow. Interaction of these discharges with solid surfaces in narrow channels, in packed bed reactors and in porous structures can greatly improve the selectivity of reaction paths by plasma driven catalysis.

2 Corona discharges

Most corona discharges have one "active" electrode with a protruding convex region of small radius of curvature that produces localized ionization close to its surface. Typical electrode configurations are thin wires in concentric cylinders or positioned between parallel planes and point electrodes facing planar or curved electrodes. The most important industrial application is in large electrostatic precipitators (ESPs) used for fly ash collection in coal-fired power plants [3]. In most cases a negative high voltage is applied to the active electrodes: straight thin wires, barbed wires or thin helical wires. Sometimes also intermittent or pulsed energization is used. The corona electrodes are mounted between parallel grounded collecting plates forming ducts through which the particle laden flue gas stream is channelled. The most important region for charging and collecting dust particles is the unipolar ion drift region connecting the minute active ionization region to the opposite electrode. In a typical flue gas the electrons formed close to the corona electrodes rapidly attach to O_2, CO_2, or H_2O molecules to form negative ions. On their way to the ground electrode these ions collide with dust particles and charge them so that electrical forces can act on them and separate them from the gas stream. In recent years pulsed streamer coronas have been propagated for the reduction of NO_x, SO_x or VOCs. The electrode configurations are similar to those used in ESPs but for this application short positive high voltage pulses are used to produce a large number of positive streamers filling most of the inter-electrode volume. In this case low energy electrons are used for excitation and dissociation of the background gas, thus producing free radicals that can be utilized for the abatement of various pollutants. Substantial improvements in pulsed power technology combined with the use of additives have led to a reduction of the specific energy requirement to values that now appear competitive [4]. Fairly large installations are already in operation for waste incineration in South

Korea and are under construction in a large power plant in Taiwan.

3 Dielectric-barrier discharges

The classical dielectric-barrier discharge (DBD), originally proposed by Siemens in 1857 for "ozonizing air", is a very elegant way to produce a non-equilibrium plasma at atmospheric pressure [1]. Several configurations using glass, ceramic, or fused silica dielectric barriers are used (Fig. 1).

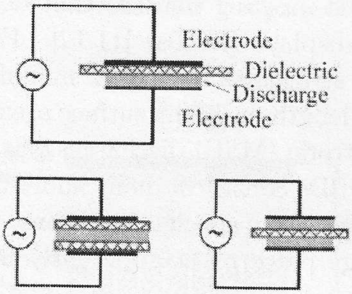

Figure 1. Common dielectric-barrier discharge configurations.

Industrial ozone generation is still a major application [5]. Most ozone generators use cylindrical glass or ceramic tubes mounted in slightly wider steel tubes, forming annular discharge gaps of typically less than 1 mm radial width through which the process gas (oxygen or dry air) flows in the axial direction. Ozone is used mainly for water treatment and increasingly also for pulp bleaching. One of the largest recent installations is that at the paper factory Votorantim Celulose e Papel (VCP), Jacarai, Brazil, which produces 500 kg ozone per hour. Modern compact ozone generators sometimes use a coplanar electrode configuration (Fig. 2) based on a design originally proposed by S. Masuda and coworkers [6,7].

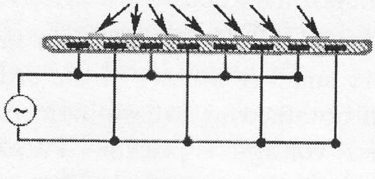

Figure 2. Coplanar DBD configuration with embedded electrodes.

Thin parallel electrode strips are embedded in a dielectric or are printed on top and covered with a thin dielectric layer. This electrode structure found large-scale industrial applications in flat plasma display panels (PDPs). Tiny gas cells, of about 0.1 mm linear dimension, filled with Xe/Ne or Xe/He at about 600 Torr are operated at a driving frequency of 100 kHz. Each pixel cell has an internal red, green or blue phosphor coating that is used to convert the VUV radiation from excited Xe atoms and Xe_2^* molecules (excimers) to the colours needed in the display [8,9,10]. Although production of flat PDPs started only in 1996 last year, 2005, already more than 7 million PDPs were sold. The annual market is expected to surpass 25 billion US by 2010. Coplanar electrode configurations are also used in another fast growing market, that of mercury-free backlighting systems for liquid crystal displays (LCDs) [11,12]. For other applications very fine meander-like electrode structures have been manufactured, occasionally with more than 1 m of electrode length on 1 cm^2 surface area. For theses discharges the term micro-structured electrode (MSE) discharges was introduced [13,14]. At atmospheric pressure most DBDs consist of many short-lived current filaments (microdischarges). Under certain, very special conditions, mainly in He, Ne, pure N_2, also self-organized discharge patterns or apparently homogeneous diffuse DBDs can be obtained [15,16].

4 Spatially confined discharges

During the last decade a number of novel discharge types were developed that can be characterized as microplasmas or discharges generated and maintained in spatially confined geometries [17,18]. Like corona discharges and DBDs these discharges can be operated at atmospheric pressure and still exhibit non-equilibrium plasma conditions. Among the most prominent representatives are microhollow cathode (MHC) discharges and cathode boundary layer (CBL) discharges proposed by Schoenbach and capillary plasma electrode (CPE) discharges investigated by Becker and Kunhardt [19,20,21]. Figure 3 shows schematic representations of these discharges. The MHC discharge in principle is based on hollow cathode discharges that have been known for a long time and that are normally operated at low pressure.

By using a thin dielectric, sandwiched between two metal foils (Fig. 3, top), and by making the hole very small (diameter of the order 0.1 mm) stable MHC discharge operation can be obtained at atmospheric pressure in various gases. Activation by dc, ac or pulsed voltages is possible. Parallel as well as series operation of MHC discharges has been demonstrated. The non-equilibrium nature was checked by measuring the gas temperature (about 2000 K), the electron density (dc about 10^{15} cm^{-3}, during short pulses up to $5 \cdot 10^{16}$ cm^{-3}) and the mean electron energy (0.5-5 eV). Numerical simulations by Kushner show that this discharge

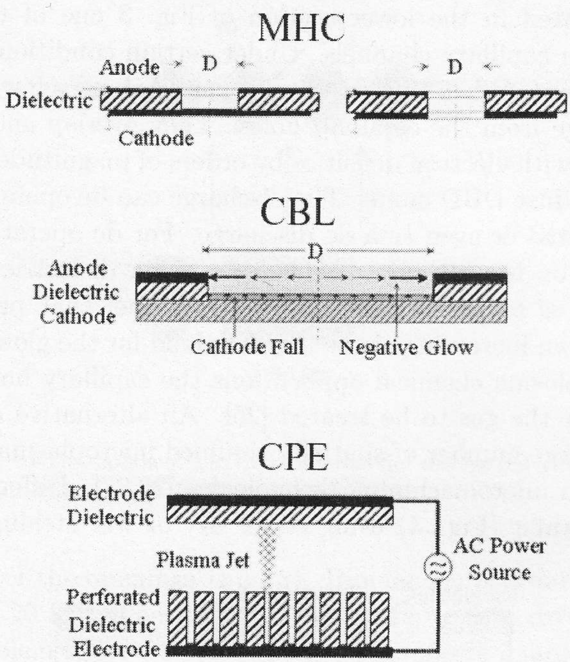

Figure 3. Microhollow cathode (MHC), cathode boundary layer (CBL) and capillary plasma electrode (CPE) discharge configurations (after K. H. Schoenbach [19], K. H. Schoenbach [20], E. E. Kunhardt [21]).

has many similarities with a glow discharge: a thin localized cathode fall region of high field strength and a moderate gas temperature [22]. If both electrodes are perforated (Fig. 3, top right) a DC MHC pumps gas through the discharge which may be utilized in plasma chemical synthesis or pollution control. Large numbers of parallel MHCs can be produced in an elegant way if perforated 70 μm thick Al foils are used and an alumina dielectric coating is prepared by anodizing the foils in an oxalic acid solution [23,24]. The process can be controlled to consistently yield Al_2O_3 films of 10 mm thickness also covering the cylindrical holes. A sandwich of two such electrodes, the upper one with round holes of 100 μm diameter, the lower one with slightly larger holes of 200 μm diameter could be operated with a 5-50 kHz sine voltage of 275 V amplitude.

The cathode boundary layer discharge shown in the middle part of Fig. 3 uses practically the same configuration but a larger round blind hole of about 1.5 mm diameter. CBL discharges exhibit a varying number of beautifully arranged self-organized bright discharge elements. Their number and configuration depends on the gas utilized, the pressure, and the current [20].

Capillary plasma electrode discharges have many similarities with conventional

DBDs. As indicated in the lower section of Fig. 3 one of the dielectrics has many parallel thin capillary channels. Under certain conditions a novel mode of operation is observed. When the frequency is raised above a few kHz tiny capillary plasma jets emerge from the capillary holes. They overlap and merge to form a volume discharge with electron densities by orders of magnitude higher then those observed in the diffuse DBD mode. The discharge can be operated also with both dielectrics perforated or even as a dc discharge. For dc operation the perforated dielectric plate is on the cathode side and the upper dielectric is removed. Each of the holes acts as a current limiting micro-channel that prevents the overall current density from increasing above the threshold for the glow-to-arc transition. With respect to plasma chemical applications the capillary holes can be used as input channels for the gas to be treated [25]. An alternative approach for mass production of a large number of spatially confined microplasmas is the utilization of available silicon micromachining technologies [26,27]. Different openings were etched into a Si wafer (Fig. 4) using either dry or wet etching techniques. The area of the inverted pyramids (left section) for example is 50 × 50 μm^2 or 100 × 100 μm^2, more recently down to 10 × 10 μm^2. A major breakthrough concerning the life expectancy of these devices was achieved, when the whole structure was covered with an additional Si_3N_4 layer of 2–4 μm thickness and the device was operated like a DBD with a 5-15 kHz sine voltage of about 200 V_{rms}. Parallel operation of several thousand discharges with a packing density of 10^4 cm^{-2} has been demonstrated.

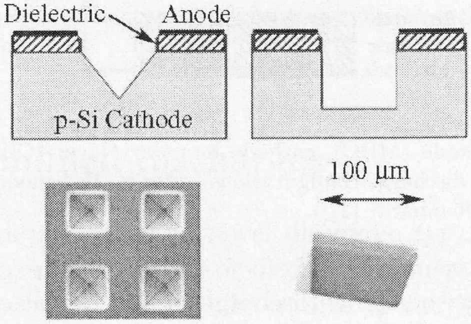

Figure 4. Si based microcavity plasma devices (after W. Frame [26], J. Chen [27]).

An alternative way to produce a large number of parallel microplasmas (Fig. 5) was proposed by the group around K. Tachibana, University of Kyoto, Japan [28,29 They use a metal mesh of 250 μm thickness containing small rectangular openings 500 × 2000 μm^2. The structure is coated with a 150 μm thick Al_2O_3 dielectric layer by plasma spraying. Two insulated Al electrodes are mounted back to back with openings aligned so that a DBD can be initiated between the plates along

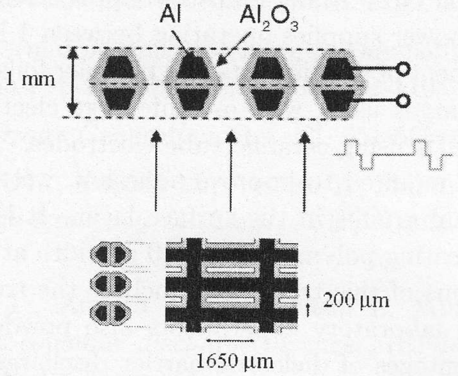

Figure 5. : Integrated coaxial-hollow micro dielectric-barrier discharges (after K. Tachibana [28] and O. Sakai [29]).

the inner surfaces of the openings (Fig. 5). Bipolar rectangular voltage pulses of 4 μs duration and 20 kHz repetition frequency are used to drive the discharges. Again, it is no problem to have simultaneous discharges in a large number of these rectangular openings in an electrode set of 5 cm diameter. At atmospheric pressure the minimum firing voltage was 500 V in He or 1200 V in N_2. The arrows in Fig. 5 indicate that a gas flow can be forced through the apertures, which turns the device into a multitude of plasmachemical microreactors.

5 Future prospects

The pronounced interest in atmospheric-pressure non-equilibrium discharges is based on the prospect to perform plasma processes normally run at low pressure without the need for expensive vacuum equipment and possibly also at a much faster rate. Another incentive is the rising interest in processes that inherently require high pressure non-equilibrium plasmas, for example processes based on three-body reactions like ozone or excimer formation. Corona discharges supplied by dc voltages use the stabilization by charges accumulated in the active ionization region to stay in the state of partial breakdown and prevent spark formation. In many applications this is a rather delicate state. With modern semiconductor technology the safe operating range of corona discharges could be considerably extended either by controlling the current or by applying short high voltage pulses. DBDs, always using alternating supply voltages, restrict the amount of charge that can be passed per half cycle and thus automatically prevent spark or arc formation. Depending on the specific application DBDs are operated with discharge gaps in the range of 0.1 mm to several cm and frequencies ranging from line frequency to several GHz. Many industrial applications now use reliable and efficient switch mode power supplies operating between 1 kHz and 500 kHz. The so-called corona treatment of plastic parts and polymer foils, historically first tried out with corona discharges using wire or knife edge electrodes, today is invariably carried out in DBDs using ceramic tube electrodes. This plasma treatment of polymer surfaces is required to improve adhesion, wettability, printability by incorporating functional groups in the surface layer. It is done on a very large scale with machines treating polymer foils of 10 m width at a speed of 100 m/min. More recent applications of this technology include the treatment of wool, other fibres and fabrics. In laboratory experiments also powders have been treated. One of the main advantages of dielectric-barrier discharges is that electrodeless systems can be designed in which no metal parts are exposed to the discharge plasma. The dielectrics used, e. g. glass, fused silica, enamel, Al_2O_3, Si_3N_4, are resistant to sputtering and have very long life expectancies. This advantage is used in excimer lamps, mercury-free excimer based fluorescent lamps, in plasma display panels and in many microcavity plasma devices.

The fast recent progress in the control of atmospheric-pressure microplasmas suggests a number of novel applications for example for selective surface modification, cleaning, etching, printing and deposition. Their use for spectroscopic analysis and biomedical diagnostics has been suggested. The small size allows on-chip chemical analysis and incorporation in miniaturized total analytical systems (μ-TAS). A number of investigations have also concentrated on the use of microplasmas as microreactors for gas phase chemistry, synthesis as well as pollution abatement and odour control. Large planar arrays of microplamas can serve as plasma electrodes to produce diffuse non-equlibrium volume discharges at atmospheric pressure. Using recent advances in the control of microplasmas and progress in micromachining and DBD excitation, glow discharges in catalyst-coated microchannels can be alternated with integrated cooling channels and thus create the possibility to combine microreactor technology with non-equilibrium plasma chemistry and catalysis [30].

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