Electrical breakdown in air: new experiments and statistical and numerical models

A P Jovanović
Department of Physics, Faculty of Sciences and Mathematics, University of Niš, Višegradska 33, P.O. Box 224, 18001 Niš, Serbia

E-mail: alexandar.bmf@gmail.com

Abstract. The electrical breakdown and discharges in air are of great significance for science and technology due to wide applications. Besides a breakdown itself, the pre-breakdown phenomena and relaxation after the breakdown have a significant role. In this report the analysis of DC glow discharge and its relaxation processes is presented. Statistical analysis of time delay distributions is presented and the statistical model based on the mixture distribution is applied to data measured with different electrodes from which electron yield is calculated. The occurrence of mixture distributions is physically explained based on analysis of the cathode surface. Also, by analyzing the memory curve measured in synthetic air the early and late relaxation of DC discharge are discussed. The processes responsible for the memory effect are identified and corresponding rate coefficients are determined. In order to confirm that the correct particles are identified, the 2D numerical model for relaxation is developed.

1. Introduction
The electrical breakdown and discharges as well as post-discharge in air are of great significance for science and technology due to wide applications for plasma devices operating in the pulsed or periodic regime, for surface treatment and modification, for plasma actuators or in medicine [1-7]. A majority of papers cover the electrical discharge in air at the atmospheric pressure [8-10], and less of them discuss low-pressure cases [11-15].

Electrical breakdown is not instantaneous process and upon application of sufficient voltage some breakdown time delay exists. The time that elapses from the moment of application of voltage greater than the static breakdown voltage \( U_s \) to the breakdown itself is the breakdown time delay \( t_d \). It consists of the statistical time delay \( t_s \) (time that elapses from the application of sufficient voltage to the appearance of the free electron that initiates breakdown) and the formative time delay \( t_f \) (time from the occurrence of initiating electron to the collapse of applied voltage and occurrence of a self-sustained current) [16]. The stochastic nature of the breakdown time delay was experimentally proven by Zuber, while von Laue derived an exponential distribution for the breakdown time delay [17, 18]. A strict mathematical transition from binomial distribution of electron occurrence in the inter-electrode space to exponential distribution for the statistical time delay was derived by Kiselev [19] and in this paper he explicitly stated that using Gaussian distribution is incorrect. Nevertheless, Gaussian and Gauss-exponential distributions of statistical time delay were obtained experimentally [14, 15, 20].

Besides the time delay distributions, the memory curve can be used for the analysis of the processes in relaxation. The memory curve was measured for the first time in the argon diode, when was noticed that the mean value of the electrical breakdown time delay depends on the relaxation time
(between the cessation of the previous discharge and the next application of the working voltage) [21, 22]. Since then, this method was used for tracing the active particle decay in afterglow of inert and molecular gases and their mixtures, including air [21-26].

In this paper the statistical analysis of the time delay distributions is presented and the mixture distribution for statistical time delay of electrical breakdown, based on the Gaussian and exponential distributions, are proposed and applied to experimental data. The relation for electron yield for cases of mixture distributions is proposed. The occurrence of mixture distributions in the case of carbon steel electrodes is explained by desorption of surface charges from the oxide on the cathode and enlarged surface area, which is confirmed by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy (AFM) measurements. By using the parameters of distribution and proposed relation, electron yield is determined. The afterglow of DC discharge in synthetic air is discussed by analysing results of the time delay measurements. The dominant processes are determined by applying analytical and numerical models and corresponding coefficients are calculated.

2. Experimental details
The time delay measurements were carried out on a gas tubes filled with synthetic air at the pressure of 300 \( Pa \). Synthetic air is a mixture of 78 percent of nitrogen with less than 5 \( ppm \) of impurities and rest of oxygen with less than 3.5 \( ppm \) of impurities. The discharge tubes are made of borosilicate glass (8245, Schott technical glass) with volume \( V \approx 300 \ cm^3 \) and with characteristic diffusion length \( \Lambda = 1.12 \ cm \). The measurements of distributions of a statistical time delay were carried out with electrodes made of carbon steel (ASTM/AISI A414E) and stainless steel (AISI 304) with diameters \( D = 6 \ mm \) and variable inter-electrode distance \( d \). Prior to instalment electrodes were lapped and polished with polishing paste with the grain size 1 \( \mu m \) and after that cleaned in ultrasonic bath in methanol and then in distilled water. The gas tube was pumped down to \( 10^{-3} \ Pa \), degassed at 650 \( K \) and then filled with the synthetic air at \( p = 300 \ Pa \). Time delay measurements were carried out with 100 data in a single series with glow time \( t_g = 1 \ s \). For the memory curve measurements only the electrodes made of stainless steel were used. The memory curve was measured by varying relaxation time \( \tau \) (afterglow period) from 1 \( ms \) to approx. 15 minutes. The tube was protected from the external light during the measurements. More details about experiment can be found in [15].

3. Analysis of statistical time delay distributions
The exponential distribution for the statistical time delay derived by Kiselev [19] covers the cases of low electron yield. The exponential distribution of statistical time delay is given by following relation:

\[
f(t_e) = \frac{1}{t_{se}} e^{-t_e/t_{se}} \quad (1)
\]

where \( t_{se} \) is the mean of statistical time delay for exponential distribution. From the parameters of this distribution the effective electron yield can be determined [18] from relation:

\[
Y_{eff} = \frac{1}{t_{se}}. \quad (2)
\]

The effective electron yield represents the electron production rate in the gas gap \( Y \) multiplied by the breakdown probability \( P \) and is given by \( Y_{eff} = YP \) [15]. Based on relation for electron yield \( Y = \gamma \Gamma S \) it is possible to estimate number density of particles that has lead to secondary electron emission (ions, residual neutral active states, etc.) where \( \gamma \) is the secondary electron yield, \( \Gamma \) is the particle flux and \( S \) is the area of the front cathode surface.

Nevertheless, in the cases of high effective electron yield, the occurrence of Gaussian and Gauss like i.e. slightly asymmetric distributions with tail are reported [14, 15, 20]. In order to physically base these distributions, the transition from binomial to Gaussian distribution is given in [14]. By using de Moivre-Laplace theorem for the cases when number of initiating electrons is very large and probabilities for occurrence and non-occurrence of effective electron is not too close to zero (i.e.
effective electron yield $Y_P$ is high), the binomial distribution of electron occurrence is approximated by the Gaussian distribution [14]. In this way the Gaussian distribution used for statistical time delay is physically based and the electron yield can be determined from parameters of the distribution. The Gaussian distribution of statistical time delay has the following form:

$$f(t_s) = \frac{1}{\sqrt{2\pi}\sigma_g} e^{-\frac{(t_s - \overline{t_g})^2}{2\sigma_g^2}}$$

(3)

from which electron yield can be determined from parameters of the distribution:

$$Y_{ef} = \frac{\overline{t_g}}{\sigma_g^2}$$

(4)

where $\overline{t_g}$ is the mean and $\sigma_g$ is the standard deviation of the statistical time delay obtained by fitting procedure [14].

In order to describe occurrence of Gauss like distributions the mixture of Gaussian and exponential distribution was proposed [20]. The mixture distribution is the mixture of two or more distributions with certain weights and in the case of statistical time delay with $n$ components has the following form [27]:

$$f(t_s) = \sum_{i=1}^{n} a_i f_i(t_s)$$

(5)

where $a_i > 0$, $i = 1 .. n$ $\sum_{i=1}^{n} a_i = 1$, $t_s$ is the statistical time delay and $a_i$ are the mixing weights. In the cases where more than one subpopulation of data exists in the whole population, the mixture distributions are often used [27, 28]. For example, the mixture distributions are applied for description of electric tubes and radio transmitter failures [28, 29], where every component in mixture corresponds to one cause of failure. In the case of statistical time delay the occurrence of mixture distributions implies on existence of more than one subpopulations of initiating electrons. For the case of statistical time delay the mixture of Gaussian and exponential distributions is first proposed in ref. [20]:

$$f_{GK}(t_s) = a_G \frac{1}{\sqrt{2\pi}\sigma_g} e^{-\frac{(t_s - \overline{t_g})^2}{2\sigma_g^2}} + a_E \frac{1}{\overline{t_e}} e^{-\frac{t_s}{\overline{t_e}}}.$$  

(6)

Since these distributions are based on binomial distribution of electron occurrence [14, 19] by starting from electron yield for Gaussian distribution, the relation for mixture of Gaussian and exponential distributions is derived [15]:

$$Y_{eff} = \frac{a_G\overline{t_g} + a_E\overline{t_e}}{a_G^2\sigma_g^2 + a_E^2\overline{t_e}^2}.$$  

(7)

This relation is more general than relations for single components and in limiting cases, when $a_G \to 0$ or $a_E \to 0$, tends to the relation for single component of mixture distribution, i.e. exponential or Gaussian one. By using proper parameters, this equation can be applied to the mixture of different components, i.e. two Gaussian distributions or two exponential distributions. Previous relation (7) can be generalized for the mixture of $n$ distributions [15]:

$$Y_{eff} = \frac{\sum_{i=1}^{n} a_i \overline{t_{si}}}{\sum_{i=1}^{n} a_i^2 \sigma_i^2}.$$  

(8)
where \( a_i \) represents the weights of components of distribution, \( \bar{t}_{si} \) is the mean value and \( \sigma_i \) is the standard deviation of the statistical time delay of a single component [15].

As example for the use of mixture distribution, the results published in [15] are presented in following text. The experimental data measured in synthetic air with carbon steel and stainless steel electrodes were analyzed and compared in order to physically explain occurrence of mixture distribution [15]. The measurements are carried out at working voltage \( U_w = 475V \), glow current \( I_g = 500\mu A \) and at glow time \( t_g = 1s \). The static breakdown voltages were \( U_s = 396V \) for the tube with carbon steel electrodes and \( U_s = 420V \) for the one with stainless steel electrodes. For the relaxation time \( \tau = 17ms \) the distribution of the data measured in the case of the sample with carbon steel electrodes has Gauss like shape (figure 1a) while the data measured in the second sample with stainless steel electrodes follow exponential distribution (figure1b). The mixture of the Gaussian and exponential distribution (6) is applied to fit the experimental data (figure 1a) and the following parameters of distribution are obtained

\[
\begin{align*}
\bar{t}_{sg} &= 4.45 \times 10^{-6} s, \\
\sigma_g &= 2.15 \times 10^{-6} s, \\
\bar{t}_{se} &= 1.02 \times 10^{-5} s
\end{align*}
\]

while the weights of distributions are fixed and chosen to be \( a_G = 0.78 \) and \( a_E = 1 - a_G = 0.22 \), respectively. From the relation (7) the effective electron yield is calculated to be \( Y_{eff} = 8.27 \times 10^{5} \, 1/s \).

The sample with stainless steel electrodes is modelled by exponential distribution (1), mean statistical time delay is determined \( \bar{t}_e = 4.23 \times 10^{-4} s \) and corresponding effective electron yield is calculated \( Y_{eff} = 236581/s \).

![Figure 1.](image.png)

The appearance of mixture distribution and increased effective electron yield indicate existence of additional initiating mechanism. The only difference between two analyzed samples is in cathode material therefore one subpopulation of electrons must originate from the surface initiating mechanism. In order to test this statement the SEM, EDX and AFM measurements are conducted (figure 2). The dark spots on SEM image (figure 2a) indicate the substance with dielectric properties, probably an iron oxide. Also, granular structure of the oxide layer can be noticed, which leads to quite enlarged effective surface area. The bright spots on the tips of granules are caused by the enhanced secondary electron emission. In EDX spectrum (figure 2b), besides iron and manganese which are constituents of the alloy, the oxygen peak is observed. Based on SEM image and EDX spectrum, it can be concluded that inhomogeneous mixture of different iron oxides is formed on the cathode surface. The iron oxide has dielectric properties and can retain surface charges. In order to better analyze the cathode surface AFM is used and from the 3d topography image (figure 2c) the characteristic granular structure similar as in SEM image is observed. The root-mean-squared (RMS) surface roughness...
$R_{RMS} = 63.23\text{nm}$ is determined for the $30 \times 30\ \mu m$ area presented in figure 2c. This confirms that high electron yield is caused by the combined effect of surface charges and enlarged effective surface area [15].

![Figure 2](image)

**Figure 2.** a) SEM image b) EDX spectrum and c) 3d topography of carbon steel cathode [15].

4. **Relaxation of DC discharge in synthetic air**

The time delay measurements are often used to analyze relaxation in various gases in order to determine the dominant processes and corresponding rate coefficients [21-26]. In this report the relaxation of synthetic air discharge is analyzed by the means of time delay measurements. The memory curve, mean time delay as a function of relaxation time $\tau$, is measured and the analytical and numerical models are applied. In figure 3 the memory curve measured on the tube filled with synthetic air at the pressure of 300 Pa, with electrodes made of stainless-steel, inter-electrode distance $d=6\ mm$, at working voltage $U_w=500\ V$, glow current $I_g=300\ \mu A$ and glow time $t_d=1\ s$ is presented. The three characteristic regions can be identified on the memory curve.

![Figure 3](image)

**Figure 3.** Memory curve measured in synthetic air at the pressure of 300 Pa, with stainless-steel electrodes, inter-electrode distance $d=6\ mm$, at working voltage $U_w=500\ V$, glow current $I_g=300\ \mu A$ and glow time $t_g=1\ s$.

The first region between $1\ ms$ and $90\ ms$ characterizes with the slow rise of mean time delay corresponding to formative time ($t_f \approx t_d$) and fast rise of mean of the statistical time delay ($t_f \approx \sigma(t_d)$). The second region from $90\ ms$ to $1000\ s$ is less steep, with the slower rise of the time delay and at the $1000\ s$ the saturation of time delay can be observed. It is assumed that in the first region the dominating particles are probably ions remained from the previous discharge. At the times...
greater than 90 ms the ion number density is most likely depleted, therefore influence of the neutral particles can be reasonable explanation of this part of memory curve. The saturation at 1000 s indicates some constant production of initiating electrons and can be explained by background radiation caused by natural radioactivity and cosmic radiation. Further, each of these regions is discussed.

The first region of the memory curve, with the fast rise of time delay, is presented in semi-logarithmic plot (figure 4), from which the three different slopes can be observed. The ions remained from the previous discharge are still present in inter-electrode space and can cause emission of initiating electrons. Based on an analytical model from [26] the connection between exponential rise of statistical time delay and diffusion losses of ionic particles is established. Therefore, this part of memory curve can be explained by change of diffusion regimes of ionic particles causing emission of initiating electrons similarly as in [26]. The characteristic decay frequencies $\nu$ are determined from the slopes, from which the effective diffusion coefficients $D_{\text{eff}} = \nu \Lambda^2$ are determined, where $\Lambda$ is characteristic diffusion length.

![Figure 4. The first region of the memory curve in synthetic air presented in semi-logarithmic plot. By using the relations shown in the figure, the connection between statistical time delay and diffusion of ions is established. The three different slopes imply existence of the change of diffusion regimes. From the relations, the effective diffusion coefficients are determined.](image)

The following step in the analysis is identification of the dominant ions leading to secondary emission of electrons. By taking into account a work function of stainless steel $e \phi_e \approx 4.5$ eV [30] and ionization energies of ions present in stable glow in synthetic air it is concluded that only $N_2^+$ ($E_i=15.57$ eV) and $O_2^+$ ions ($E_i=12.5$ eV) [31] can lead to secondary electron emission. However, from the rate coefficient for conversion of $N_2^+$ into $O_2^+$ ion ($\approx 6 \times 10^{-11}$ cm$^3$/s), it can be concluded that $N_2^+$ density must fall earlier than $O_2^+$ density. Therefore, $O_2^+$ ion is dominant in this part of memory curve. The reasonable agreement of determined diffusion coefficients with the ones from other experiments is reached (i.e. 690 cm$^2$/Torr/s at the electron temperature 4000K measured in time interval from 0.7 to 3 ms which gives 52 cm$^2$/Torr/s at 300 K in ref. [12] and 122 cm$^2$/Torr/s in time interval from 0.02 to 0.5 ms in ref. [13]). In order to confirm previous analysis, 2D numerical model is developed and applied.

The two-dimensional model for relaxation, consisting of diffusion equation with productions and losses of corresponding particles, is solved in cylindrical coordinates in order to describe afterglow in synthetic air:

$$\frac{\partial n}{\partial t} - D \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial n}{\partial r} \right) + \frac{\partial^2 n}{\partial z^2} \right] = S$$

(9)

where $n$ is the particle number density (electron, ion or neutral), $D$ is the diffusion coefficient and $S$ is the term representing productions and losses of corresponding particle in relaxation. The system of
differential equations is discretized by using the implicit finite difference method. System of equations is further solved by a successive over relaxation (SOR) method. The used mesh has $30 \times 30$ nodes, while time and spatial steps are set to be $dt = 10^{-7} \ s$ and $dr = dz = 0.1 \ cm$, respectively. Model includes 5 ionic species $N_2^+$, $O_2^+$, $N_2^+$, $O_2^+$, $O^-$, metastable states $N_2(S^+_3)$, $N_2(S' ^1)$ and $N$ and $O$ atoms. The model includes 25 processes of dominant particles with rate coefficients taken from refs. [32-34], where the most dominant process is conversion of nitrogen ions in oxygen ions. The diffusion and mobility data for ions were taken from [35-37] and for neutral particles were calculated from relation given in ref. [38]. The variation of $N$ and $O$ atom number densities in early relaxation is neglected in order to speed up the calculations.

![Figure 5](image.png)

**Figure 5.** Axial number density profiles of ionic species in stable glow discharge in synthetic air obtained from the one-dimensional fluid model used as initial densities for modelling of relaxation.

The initial densities are calculated from a one-dimensional fluid model consisting of the zero momentum (particle continuity equation) of Boltzmann’s equation and Poisson equation in which all relevant particles for the afterglow are included as well as ionization terms as described in [39]. The stationary densities of charged particles in glow discharge are used as initial densities for modelling of the relaxation are determined (figure 5). Based on the calculated stationary axial profiles, the initial two-dimensional profiles in the tube are calculated by “filling up” the tube where the densities inside inter-electrode space are taken as a constant and 2D model was running until the stationary densities in whole tube are obtained. Since at these pressures and relaxation times the diffusion losses are dominant, in order to fit the experiment different relations for the change of diffusion regimes were used. For the transition regime of electron diffusion the following relation was used [40]:

$$D_{se} = D_a \left( \frac{D_e + \Lambda^2 n_e \mu_e / \varepsilon_0}{D_a + \Lambda^2 n_e \mu_e / \varepsilon_0} \right)$$ (10)

where $D_a = (\mu_e / \mu_i) D_e$ is ambipolar diffusion coefficient, $n_e$ is electron number density, $\Lambda$ is characteristic diffusion length of the tube, $\mu_e$ is electron mobility, $\mu_i$ is mobility of dominant $O_2^+$ ion, $\varepsilon_0$ is vacuum permittivity and $e$ is elementary charge. When the ratio of characteristic diffusion length and Deby radius $\lambda_D$ falls to $\Lambda / \lambda_D < 100$, the diffusion regime changes into transition regime and for ions is given by the following relation for effective diffusion coefficient [41, 26]:

$$D_{\text{eff}} = D_i \left(1 + \frac{T_e}{T_i} \right).$$ (11)

where $D_{\text{eff}}$ is effective diffusion coefficient, $D_i$ is ion free diffusion coefficient, $T_e$ is electron temperature and $T_i$ is ion temperature (equal to gas temperature $T_g$). In order to correctly describe the electron temperature decay, the two-exponential decay was used, where slowed down decay due to superelastic collision with metastables and vibrational excited states was assumed, similarly as in pure
nitrogen [42]. Finally, the last part of memory curve was fitted with the effective diffusion coefficient dependence $D_{\text{eff}} \sim \Lambda / \lambda_{\text{D}}$.

Figure 6. a) The evolution of particle number densities in relaxation and b) the electron yield (symbols) fitted with the numerical model where (dashed line) is contribution of ionic particles and (solid line) sum of contributions.

From the figure 6a it can be seen that due to intensive conversion of nitrogen ions the dominant particles in early relaxation are oxygen ions, i.e. $O^+_2$ and $O^+_4$ ion. The experimental data for electron yield are fitted well with diffusion loss of this ion (figure 6b). The discrepancy noticed in the first several milliseconds is most probably caused by the influence of formative time. At around 60 ms the contribution of neutral particles had to be included to describe experimental data because ion density has fallen at these relaxation times. Since the of neutral particles slowly decrease, contribution is almost constant, the fall of ions contribution of electron yield still describes fall of total electron yield.

Figure 7. The linearization of a) square root of mean time delay as a function of relaxation time and b) mean time delay as a function of relaxation time.

The second part of memory curve is in interval 90 ms-1000 s in which number densities of the ionic species are depleted, therefore only neutral particles (most probably nitrogen atoms) can lead to emission of initiating electrons. In the ref. [25] the memory effect in pure nitrogen with the iron cathode is explained by the surface recombination of nitrogen atoms. Based on recombination energy of nitrogen and oxygen atoms it is more probable that nitrogen atom recombination is responsible for the memory effect in synthetic air, like in the case of pure nitrogen [25]. At our conditions the volume recombination of nitrogen atoms is negligible (volume recombination coefficient $\sim 10^{-34} \text{cm}^3 / \text{s}$), hence only possible loss process is surface recombination. By linearizing the data in corresponding
plots [25], the order of reactions is determined (figure 7). The two different slopes indicate change of mechanisms i.e. change of the second order into the first order surface recombination.

![Figure 8](image)

**Figure 8.** The experimental data for electron yield in relaxation and numerical fit calculated from the 2D numerical model. The relations for electron yield used to fit the experimental data are given in the figure ([N] is number density of nitrogen atoms in front of the cathode surface). The first part of curve in late relaxation is explained by the second order recombination of nitrogen atoms on the cathode and after 6 s the first order recombination becomes dominant.

In order to better describe late afterglow in synthetic air, the two-dimensional model is developed. It consists of diffusion equation (9) for nitrogen atom with included surface loss processes. The equation is discretized with explicit finite difference method. By using the recombination coefficient on glass walls $\gamma_{NW} = 4 \times 10^{-11} \text{ cm}^3 / \text{s}$, as well as the second order recombination coefficients on electrodes, satisfactory agreement with the experiment is reached (figure 8). The values of surface recombination coefficients on glass are larger, while the surface recombination coefficients on cathode are lower in comparison to values determined in nitrogen [25], which can be explained by the presence oxygen atoms in air and different cathode material (i.e. stainless steel and iron). The change of order is explained with the fall of nitrogen atom density.

5. Conclusion

The analysis of statistical time delay distributions and memory curve measured in synthetic air is presented. The relations for mixture distributions of statistical time delay and for electron yield are generalized starting from a binomial distribution of initiating electron occurrence. The memory effect in synthetic air is explained with diffusion losses of $O_2^-$ ion as well as surface recombination of nitrogen atoms and corresponding coefficients were determined.

Acknowledgments

The author is grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for the financial support (project ON171025), M. Miljković for SEM and EDX and R. Gajić and B. Vasić for AFM measurements.

References

[1] Shao T, Sun G, Yan P, Wang J, Yuan W, Sun Y and Zhang S 2006 J. Phys. D: Appl. Phys. 39 2192
[2] Fang Z, Qiu Y and Kuffel E 2004 J. Phys. D: Appl. Phys. 37 2261
[3] Pandiyaraj K N, Selvarajan V, Deshmukh R R, Yoganand C P, Balasubramanian S, Maruthamuthu S 2013 Plasma Sci. Technol. 15 56
[4] Shin J, Narayanaswamy V, Raja L L and Clemens N T 2007 AIAA Journal 45 1596
[5] Soloshenko I A, Tsiolko V V, Khomich V A, Shchedrin A I, Ryabtsev A V, Bazhenov V Yu and Mikhno I L 2000 Plasma Phys. Rep. 26 792
[6] Kutasi K, Pintassilgo C D, Coelho P J and Loureiro J 2006 J. Phys. D: Appl. Phys. 39 3978
