The Plasma Chemistry of Electrical Breakdown in Air

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Abstract: It is proposed that breakdown in air is initiated by plasma chemistry changing the composition of air through the production of metastables rather than being initiated by either the Townsend mechanism of electrode effects, or the streamer mechanism of space charge effects. Metastable vibrational states of nitrogen can increase the ionisation coefficient by a factor of 1000 at low $E/N$, which coupled with electron detachment from ions by metastable $a^1\Delta_g$ states of oxygen molecules, lowers sustaining electric fields from 25 to 5 kV/cm.

Keywords: vibration nitrogen states, singlet delta oxygen states, electrical breakdown, Townsend, streamer.

1. General

It has been fairly common to view electrical breakdown in air as a sudden transition producing a hot arc, initiated by the requirement of either the Townsend breakdown criterion of electrons at the cathode being replaced by secondary processes such as photo-emission or ion bombardment [1], or by the onset of space charge effects, as indicated by the streamer breakdown criterion [2].

In Section 2 it is shown that neither the Townsend criterion, nor the streamer space charge criterion, conforms to observations of the initiation of corona. The view of the present paper is that breakdown to form a hot thermal arc is only the third of three fairly separate stages. The first is the stage of a “Townsend discharge” where electrons move in air obeying the regular coefficients formulated by Townsend of electron ionisation, attachment, drift and diffusion. Then there is a second stage, intermediate between the Townsend and arc discharge, where the actual composition and properties of air are changed, predominately by the existence of metastable states of nitrogen and oxygen. This stage has been described as the glow or streamer stage. Effective ionisation and attachment coefficients then differ by orders of magnitude from the Townsend regime.

The properties of this second stage differ in three marked respects from the first stage. (1) The sustaining electric field at 1 bar is ~5 kV/cm, rather than 25 kV/cm. (2) The discharges are generally pulsed; successive pulses either originate from the same point on an electrode, as in corona discharges, or are stepped, as can occur in lightning, where successive pulses start at the end point of the preceding pulse. (3) Unlike Townsend discharges, space charge effects occur.

Corona onset fields are discussed in Section 2, and correspond to a Townsend discharge. Effects where there are significant vibrational states of nitrogen molecules, discussed in Section 3, and significant singlet delta states of oxygen, discussed in Section 4, correspond to a glow or streamer discharge. The total breakdown process to form the third stage of an arc is discussed in Section 5.

2. Corona onset

Figure 1 shows experimental values of the fields at the surface of a cylinder for the onset of corona obtained by various experimentlists [3]. Also shown on the figure are curves of the calculated total avalanche size, $Q$, that would be developed by a single electron starting at the surface of the cylinder and moving perpendicular to the cylinder. The path length is over the region for which there is net positive ionisation. $Q$ is obtained from

$$Q = \exp\left(\int (\alpha - \eta)dr\right).$$

where $r$ is the radius, $\alpha$ is the ionisation coefficient and $\eta$ the attachment coefficient. It is seen that the curve of $Q = 10^4$ gives a reasonable fit for cylinders with radii of curvature varying from 0.01 cm to 30 cm. Furthermore a curve of $Q = 10^4$ fits measured values for the onset of corona at spheres and points for a similar range of radii [3].

The results suggest the onset of a process in the air itself occurring after only the order of $10^4$ ionising events. The experimental results of onset
electric fields have been found by various investigators to be independent of the polarity of the corona voltage. Thus, contrary to the Townsend process, the corona onset is independent of the electrode, particularly as for corona, a change in polarity means that the cathode is composed of air rather than metal. Furthermore, the streamer breakdown criterion based on space charge effects requires an avalanche size of \( \sim 10^8 \) [2], so that the streamer theory also does not explain the experimental results for corona onset.

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Figure 1. Experimental data points for the onset of corona from wires compared with calculated curves of the size of an avalanche developed from a single electron starting at the wire surface; from [3].

### 3. Nitrogen vibrational states

It is proposed that principal properties of the glow or streamer state, such as the markedly increased electrical conductivity, can be explained by processes of plasma chemistry involving the excitation of the metastable vibrational states of nitrogen and the singlet delta metastable state of oxygen. For electron motion in air for the Townsend state, excitation of the many vibrational states of nitrogen is initially the principal energy loss process, as shown in Figure 2. The curves also show excitation rates for the total of the electronic nitrogen states and for ionisation and attachment.

There are approximately 60 vibrational states associated with the electronic ground state of nitrogen. The excitation energy of the first state is 0.29 eV, but the 60th state extends to energies of the order of 8 eV, as are shown in the energy level diagram of Figure 3. As these states are metastable, and their lifetime is of the order of 1 ms, compared with the breakdown process of usually less than a microsecond, their populations accumulate from reaction (1). Furthermore higher energy states are excited through successive electron collisions of reactions (1) and (2). These states also accumulate through collisions among themselves, as in reactions (3) and (4).

\[
e + N_2 \rightarrow e + N_2^* \quad (1)
\]
\[
e + N_2^*(v) \rightarrow e + N_2^*(v+1) \quad (2)
\]
\[
N_2^*(v) + N_2 \rightarrow N_2^*(v+1) + N_2^*(v-1) \quad (3)
\]
\[
N_2^*(v) + N_2 \rightarrow N_2^*(v-x) + N_2^*(x) \quad (4)
\]

The vibrational densities and vibrational temperatures of these states increase until they come into approximate equilibrium with the electron density and the electron temperature. Measurements recently obtained using spontaneous Raman spectroscopy and coherent anti-Stokes Raman spectroscopy have measured vibrational temperatures of the order of 7000 K formed after only 20 ns of the commencement of discharges in air and nitrogen, with translational and rotational temperatures still being close to the ambient temperatures of \( \sim 300 \) K [4,5].

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Figure 2. Excitation rates in air for the sum of (a) vibrational and (b) electronic molecular states of nitrogen together with ionisation and attachment rates.

Figure 3. Energy levels of nitrogen molecules; from [7].
At equilibrium, there are then approximately as many collisions of metastables with electrons in which electrons gain energy by de-exciting metastables, as there are collisions of electrons losing energy through the excitation of metastable states. As a consequence, low energy electrons gain energy in collisions with excited vibrational states, as in reaction (5), thus increasing the number of electrons with energy sufficient to cause ionisation.

\[ \text{N}_2^*(v) + e \rightarrow \text{N}_2^*(v-1) + e \]  \hspace{1cm} (5)

Calculations made of the consequent changes to the electron energy distribution function using the computer code ELENDIF [6] are shown in Figure 4 for \( E/N = 20 \text{Td} \). As a consequence, ionisation coefficients at low values of \( E/N \) are increased by up to three orders of magnitude, as shown in Figure 5; \( E \) is the electric field, \( N \) the gas number density, and \( 1 \text{Td} = 10^{-17} \text{ V cm}^2 \).

The calculations of Figures 4 and 5 are for an \( E/N \) of 20 Td, for which at 1 bar the field is 5 kV/cm. Collisions of the excited vibrational states with low energy electrons result in heating of these electrons and, remarkably, the vibrational states instead of causing an electron energy loss, are a process of electron energy gain [7]. The calculations of Figures 3-5 require cross sections of the collision processes which have been taken from [8] for nitrogen and [9] for oxygen; there being nine cross sections for vibrational excitation of nitrogen and eight for oxygen.

4. Singlet delta oxygen molecular states

Electrons, on colliding with oxygen molecules produce the singlet delta metastable state \( (a^1\Delta_g) \), as in reaction (6), and these states have a lifetime in air at 1 bar of approximately 100 ms [10]. This metastable state has the well-established property of detaching negative oxygen ions to produce electrons, as in reaction (7) [11]. Calculations of the excitation coefficients \( m \), of the singlet delta metastables are shown in Figure 6, taken from [12], again using the cross sections of [8] and [9].

\[ \text{e} + \text{O}_2 \rightarrow \text{e} + \text{O}_2 (a^1\Delta_g) \]  \hspace{1cm} (6)

\[ \text{O}_2 (a^1\Delta_g) + \text{O}_2^- \rightarrow \text{e} + 2 \text{O}_2 \]  \hspace{1cm} (7)

The growth of an avalanche from a single electron along a path length from the surface of a cylinder of radius 0.1 cm is shown in Figure 7 for various values of the initial electric field at the surface of the cylinder. The broken curves show calculations without the influences of metastable de-excitation or electron detachment from negative ions. It is seen that these effects cause a marked increase in ionisation from radii of 0.1 mm to about 0.8 mm because of their increase in net ionisation to much lower electric fields than 25 kV/cm. The
rate coefficient for reaction (4) was set at 1/200 of electron vibrational excitation of Figure 2.

![Figure 7](image)

Figure 7. Calculated avalanche sizes that develop at the surface of a cylindrical wire of diameter 0.1 cm for various surface electric fields.

The coupled influences of the detachment of electrons from negative ions by oxygen metastables and the enhanced ionisation due to the de-excitation of nitrogen metastables have the effect of significantly lowering the electric field required to sustain an electric discharge. A similar reduction in electric field has been calculated previously [12] from enhanced ionisation coefficients for values of $E/N$ between 20 Td and 70 Td which happen to be approximately equal to those of Figure 5 for 20000 K. These sustaining fields are calculated as a function of current density by solving the time-dependent equations for the particle densities of ions, metastables and electrons as a function of current density. The calculated reduced sustaining electric fields are shown in Figure 8, and it is seen that fields as low as 5 kV/cm are possible, consistent with experimental evidence that such low fields can sustain glow discharges in air [7].

![Figure 8](image)

Figure 8. Calculated electric fields as a function of current density, accounting for detachment, metastable quenching, ionisation, attachment and recombination; from [12].

The complete plasma chemistry of this system is very complex. Further calculations are needed on other metastable interactions, effects of molecular excited states, and quenching effects from O and N atoms. Furthermore, in another investigation, Naidis has presented calculations supporting the very different explanation that the onset of positive corona after avalanches of a size of only $10^4$ is due to photo-ionisation [13].

5. Summary of the breakdown process in air

Electrical breakdown to form an arc in air at 1 bar is regarded as consisting of three separate processes. Firstly, a Townsend discharge develops from an avalanche from a single electron which grows to the size of about $10^4$. Second, a glow or streamer stage develops from the influence of metastable nitrogen and oxygen molecules which reduce the discharge sustaining field to ~5 kV/cm instead of the 25 kV/cm that exists for the first stage. There are then influences from space charge effects from the discharge and electrode effects fulfilling the Townsend breakdown criterion, so that heating causes an electric arc to form in the third stage, for which the sustaining electric fields are of the order of only 0.02 kV/cm.

6. References


7. Acknowledgements

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