41. REPETITIVELY-PULSED GLOW DISCHARGE IN ATMOSPHERIC PRESSURE AIR: MODELING AND EXPERIMENTS

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Abstract. Diffuse glow discharges were produced in low temperature (<2000 K) atmospheric pressure air with electron number densities in excess of $10^{12}$ cm$^{-3}$, more than six orders of magnitude higher than in thermally heated air at 2000K. The measured discharge characteristics compare well with the predictions of a two-temperature kinetic model. Experimental and modeling results show that the steady-state electron number density exhibits an S-shaped dependence on the electron temperature, a behavior resulting from competition between ionization and charge transfer reactions. The power requirements of DC discharges at atmospheric pressure can be reduced by several orders of magnitude using short repetitive high-voltage pulses. Between consecutive pulses, the plasma is sustained by the finite rate of electron recombination. Repetitive discharges with a 100kHz, 12kV, 10ns pulse generator were demonstrated to produce over $10^{12}$ electrons/cm$^3$ with an average power of 12W/cm$^3$, 250 times smaller than a DC discharge at $10^{12}$/cm$^3$.

Introduction

There are interesting applications of nonequilibrium diffuse discharges in molecular gases, particularly air, at atmospheric pressure. Desirable conditions are electron densities greater than $10^{12}$cm$^{-3}$ at gas temperatures less than 2000K. To increase the electron number density without significantly heating the gas, energy must be added in targeted fashion. One method is to apply the energy addition to the free electrons by means of an electrical discharge. Such discharges have been successfully applied in atmospheric pressure air [1] to produce stable, diffuse plasmas with electron densities of up to $10^9$cm$^{-3}$, but higher electron densities are considered difficult to obtain owing to instabilities and arcing effects [1].

In this paper, we first describe our two-temperature chemical kinetic models of air plasma discharges. We then present results of experiments in atmospheric pressure air, using either cold or preheated process gas, in which the electron density was raised to above $10^{12}$cm$^{-3}$ by means of a DC discharge. Finally, we present results from pulsed discharge experiments in which electron densities of more than $10^{12}$cm$^{-3}$ in air are produced with approximately 12W/cm$^3$, a factor 250 times lower than the power required for a DC discharge.

Two-Temperature Kinetic Models

Two-temperature chemical kinetic models were developed to understand the mechanisms governing ionization and electron recombination in discharges produced by an applied electric field. The two temperatures are the electron temperature, $T_e$, and the gas temperature, $T_g$. Rate coefficients describing the air plasma chemistry were derived using the Weighted Rate Coefficient (WRC) method presented in [2]. In this method, rate coefficients are calculated as a weighted average of elementary rates over the internal states of atoms and molecules. Elementary rate coefficients are calculated from cross-section data assuming Maxwellian velocity distribution functions for electrons and heavy-particles, and are then averaged over the internal energy levels, assuming Boltzmann distributions at the electronic temperature $T_{el}$, vibrational temperature $T_v$, and rotational temperature $T_r$. It is further assumed that $T_{el}=T_e$ and $T_r=T_g$. The remaining parameter, $T_v$, can only be determined by means of a collisional-radiative (CR) model of vibrationally-specific state-to-state kinetics. We have developed a CR model to determine the relation between $T_v$ and $T_g$ and $T_e$ in atmospheric pressure nitrogen plasmas [3]. It was shown [4] that the steady-state concentrations determined with a two-temperature kinetic model assuming $T_v=T_g$ are in close agreement with the CR model predictions in the range of electron densities of interest here, and are at worse within a factor 5 of the CR model predictions at electron densities greater than about $10^{17}$cm$^{-3}$ (region B in Fig.1). In contrast, the often-used assumption $T_v=T_e$...
would produce steady-state electron number densities several orders of magnitude greater than those obtained with the CR model at the electron densities of interest. We extend these results to atmospheric pressure air by calculating all WRC rate coefficients with the assumption $T_e=T_g$. Two-temperature kinetic calculations were made with the CHEMKIN solver [5] modified to account for two-temperature rates [6]. Electron attachment reactions are neglected because the equilibrium concentrations of $O_2^+$ and $O_3^+$ are negligible relative to the concentration of electrons in atmospheric pressure air above $\sim1500K$.

**Two-temperature chemistry simulations**

We consider first the case of an air plasma in equilibrium at 2000K and 1atm at time zero when an elevated electron temperature is instantaneously prescribed, in an idealized way modeling an electrical discharge in a reactor section. Species concentrations are calculated for various electron temperatures while keeping the gas temperature constant at 2000K. For $T_e \geq 6000K$, electron-impact ionization reactions become important and the steady-state electron number density increases rapidly with the electron temperature. The small circles in Fig.1 represent the predicted steady-state electron number densities as a function of the electron temperature in atmospheric pressure air at fixed $T_g=2000K$. An abrupt decrease in electron density occurs for $T_e \geq 17,000K$ where the predicted steady-state electron number density suddenly increases by the same processes as in the reverse case where steady-state electron concentrations are calculated from an initial composition given by the steady-state solution at $T_g=2000K$ and $T_e=22,000K$ (corresponding to $n_e(r=0) \geq 10^{15}cm^{-3}$), the predicted steady-state electron number densities (large circles in Fig.1) start by decreasing along the same upper curve as in the previous case, but instead of the abrupt decrease at $17,000K$, continue their smooth decrease until the electron temperature reaches $\sim14,000K$. When $T_e$ is further decreased below $14,000K$, the steady-state electron density abruptly decreases and then retraces the solution of the previous case. Thus the electron number density as a function of the electron temperature presents a hysteresis. Detailed examinations of the mechanism and rates were made to determine the main reactions controlling the steady-state electron number density in regions A and B [6]:

**Region A:** When the electric field is applied, the electron concentration rises rapidly as a result of three-body electron-impact ionization of $N_2$ and $O_2$, and of electron-impact dissociation of $O_2$ followed by electron-impact ionization of $O$. The charged species produced by these processes undergo rapid charge transfer to $NO^+$, mainly via $O^+ + N_2 \rightarrow NO^+ + N$. The main electron removal reaction is the two-body dissociative recombination reaction $NO^+ + e \rightarrow N + O$. When the concentration of $NO^+$ becomes sufficiently large, the rate of dissociative recombination balances the rate of electron production and the plasma reaches steady state. Thus in Region A, the termination step of the ionization process is the two-body recombination of a molecular ion.

**Region B:** The initial electron number density increase occurs by the same processes as in region A, i.e. electron-impact ionization of $N_2$, $O_2$, and $O$. Unlike in Region A, however, charge transfer reactions are not fast enough to produce sufficient $NO^+$ for the rate of dissociative recombination to balance the ionization rate. This is because the latter reactions are controlled by the gas temperature, whereas electron-impact ionization reactions are controlled by $T_e$. The limit between Regions A and B corresponds approximately to the electron temperature for which the rate of the charge transfer reaction $O^+ + N_2 \rightarrow NO^+ + N$ is comparable with the rate of avalanche ionization by electron impact. Above this critical electron temperature, the avalanche ionization process continues until all molecular species are dissociated. Eventually the rates of three-body electron recombination reactions balance the rate of ionization, and steady state is reached.

**Analytical solution:** The kinetics in Regions A and B can be described with a simplified subset of reactions that take into account the dominant channels discussed in the foregoing section. With this simplified mechanism, the steady-state concentrations of major species are obtained by solving the species conservation equations of electrons, $O_2$, $O$, $NO^+$, $O^+$, $O_3^+$, and $N_2^+$. By elimination of $n_{O_2}$, $n_{O_2}$, $n_{O_2}$, $n_{O_2}$, $n_{N_2}$, and $n_{NO^+}$, a tenth degree polynomial in $n_e$ is obtained, with coefficients that only depend on $T_p$, $T_e$, $n_{O_2}$, and $n_{N_2}$. The roots of this polynomial are plotted in Fig.1 along with the CHEMKIN predictions obtained with the full kinetic mechanism. For comparison with the kinetic model, the “S-shaped” curves of $n_e$ vs. $T_e$ have been converted into more readily measured current density vs. electric field by use of Ohm’s law and the electron energy equation. The latter incorporates the results of the collisional-radiative model to account for non-elastic energy losses from the free electrons to the molecular species. The electrical discharge characteristics of Fig.4 in the following section exhibit variations that reflect both the S-shaped
dependence of electron number density versus $T_e$, and the dependence of the inelastic energy loss factor on the electron temperature and number density.

**DC Discharges**

To test the predicted S-shaped curve, DC discharge experiments were conducted with atmospheric pressure flowing air plasmas. The experimental setup is shown in Fig.2. Process gas is injected in the discharge region with low initial electron density. Spectroscopic and electrical measurements are made of the temperature, electrical conductivity and electron density as a function of the applied discharge current.

**DC Discharge Experiments in Air**

Fig.3a shows a photograph of the air plasma plume at a temperature of approximately 2000K in the region between the two electrodes without the discharge applied. Fig.3b shows the same region with a DC discharge of 5.2kV and 200mA applied. The interelectrode distance is 3.5cm. The bright center region in Fig.3b corresponds to the discharge-excited plasma. The discharge diameter is approximately 3.2mm (at half-maximum intensity) and the electron concentration determined from electrical conductivity measurements is approximately $10^{12} \text{cm}^{-3}$. The temperature profile was measured from rotational lines of the $OH$ (A-X) transition in the case without the discharge, and of the $N_2$ (C-B) transition with the discharge applied. The centerline temperature decreases from 2300K at the cathode to 2020K at the anode when no discharge is applied. With the discharge, the measured temperature remains approximately constant at 2300K along the discharge axis. Radial temperature profiles measured at 1.5cm downstream of the cathode are shown in Fig.3c. It appears that the discharge does not noticeably increase the rotational temperature of the plasma under these conditions.

The measured discharge characteristics for plasma temperatures ranging from 1800 to 2900K are shown in Fig.4. Also shown are the predicted discharge characteristics at temperatures of 2000 and 3000K. A more detailed description of our theoretical work on discharge characteristics may be found in [6]. Good agreement is obtained between the measured and predicted discharge characteristics over a range of experiments.
spanning over three orders of magnitude in current density.

Fig.4. Measured (symbols) and predicted DC discharge characteristics in air at 1 atm

Pulsed Discharges

As the power required to sustain elevated electron densities with DC discharges is large, a power reduction strategy based on pulsed electron heating was explored. This strategy is illustrated in Fig.5. Short voltage pulses are applied to increase the electron number density. After each pulse, $n_e$ decreases according to electron recombination processes. When $n_e$ reaches the minimum desired value, a second pulse is applied. The average electron density obtained with this method depends on the pulse duration, pulse voltage, and the interval between pulses. This approach is analogous to the pulsed discharges of [7,8], which operated at lower pressures and lower electron densities in CO$_2$-laser mixtures.

Fig.5. Repetitively pulsed strategy

As seen in the previous section, DC discharges can maintain $n_e \geq 10^{15}$ cm$^{-3}$ in atmospheric pressure air with electric fields producing an electron temperature on the order of 1 eV. To produce the same average electron density with short (1-10ns)-pulsed discharges, a higher electron temperature of about 3-5eV is required. Although the corresponding field is higher than for a DC discharge, the ionization efficiency is much larger in the pulsed case than in the DC case because the energy lost to nitrogen molecules, per electron created, is several orders of magnitude smaller at $T_e=3-5$eV than at 1eV. This coupled with the finite electron recombination time allows the power budget to be dramatically reduced with pulsed discharges. It may be shown [9] that the power reduction afforded by the repetitively pulsed approach relative to DC is given by:

$$R \approx \frac{k_{ion}(T_{e,Pulse})N}{k_{DR}n_e^2} (e^{-2} \alpha^*(a_1)^2 \left( \frac{T_{e,DC}}{T_{e,Pulse}} \right)^{3/2}}$$

where $\alpha=\alpha_k N \tau_l$, and where $k_{ion}$ is the species-weighted rate coefficient for electron impact ionization of O$_2$, N$_2$, and O, $k_{DR}$ the rate coefficient for dissociative recombination of NO$^+$, $N$ the total number density of species, $\tau_l$ the pulse length, $n_e^*$ the average electron number density produced by the repetitively pulsed discharge, and $T_{e,DC}$ and $T_{e,Pulse}$ represent the electron temperatures produced by the DC and pulsed discharges, respectively.

Experiments with a Single Pulse

To test the pulsing scheme, experiments were conducted [9] in atmospheric pressure, 2000K air using a pulse forming line capable of generating a 10 ns rectangular pulse with peak voltage up to 16kV.

To experimentally simulate the conditions of a repetitively pulsed discharge, the initial elevated electron number density generated by the “previous” pulse is created by means of a DC discharge in parallel with the pulser. The circuit schematic is shown in Fig.6. With a DC voltage of 2kV and current of 150mA, the initial electron density is $6.5 \times 10^{11}$ cm$^{-3}$. A 10kV, 10ns pulse is superimposed to further increase the electron density. The measured discharge diameter of about

Fig.6. Schematic of the combined pulsed and DC discharge experiments
3mm is comparable with the diameter of the DC discharge (Fig.7). The temporal variation of plasma conductivity was measured from the voltage across the electrodes and the current density through the plasma. The electron density increases from $6.5 \times 10^{11}$ to $9 \times 10^{12}$ cm$^{-3}$ during the pulse, then decays to $10^{12}$ cm$^{-3}$ in about 12 μs (Fig.8). The average measured electron density over the 12 μs duration is $2.8 \times 10^{12}$ cm$^{-3}$.

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Figure 8 shows a comparison of the measured electron number density with the predictions of our two-temperature model. The predictions agree well with the measured electron decay time of 12 μs. This decay time is consistent with the dissociative recombination time of NO$^+$ predicted to be 8.7 μs without the DC background. Thus these results provide validation of our chemical kinetic model of the recombination phase.

**Experiments with 100 kHz Repetitive Discharge**

The success of the proof-of-concept experiments conducted with the single pulse discharge led us to investigate the generation of air plasmas with a repetitively pulsed discharge. A repetitive pulser capable of generating 10ns pulses, with peak voltages of 3-12kV and pulse repetition frequencies up to 100kHz was acquired from Moose-Hill/FID Technologies. This pulser operates with a solid-state opening switch or Drift-Step Recovery Diode (DSRD). The experimental set-up is shown in Figs.9 and 10. The discharge is applied to preheated, LTE air at atmospheric pressure and 2000 K.
atmospheric pressure preheated (2000K) air is shown in Fig.11.

![Image](image1.jpg)

**Fig.11.** Photograph of repetitive pulse discharge in air at 2000K, 1 atm

The diffuse character of the discharge was confirmed with time resolved (1.5 ns frames every 2ns) measurements of plasma emission during the pulse. The diameter of the discharge is approximately 3.3mm. Fig.12 shows the measured temporal variations of the electron density during three cycles of the pulsed discharge. The electron number density varies from $7 \times 10^{11}$ to $1.7 \times 10^{12}$cm$^{-3}$, with an average value of about $10^{12}$cm$^{-3}$.

![Image](image2.png)

**Fig.12.** Electron number density measurements in the repetitively pulsed discharge.

The power deposited into the plasma by the repetitive discharge was determined from the pulse current (measured with a Rogowski coil), the voltage between the electrodes (6kV peak) minus the cathode fall voltage (measured to be 1525V by varying the gap distance), and the measured discharge diameter. The peak pulse current was 240mA. The power deposited is found to be 12W/cm$^3$, consistent with the theoretical value of 9W/cm$^3$ for an optimized pulsed discharge producing $10^{12}$ electrons/cm$^3$. It is lower, by a factor of 250, than the power of 3000W/cm$^3$ required to sustain $10^{12}$ electrons/cm$^3$ with a DC discharge.

**Conclusion**

Two-temperature ($T_e > T_g$) kinetic models accounting for ionizational, chemical, vibrational and electronic nonequilibrium, and incorporating a collisional-radiative model with over 11,000 transitions have been developed to understand the mechanisms of ionizational nonequilibrium in atmospheric pressure air electrical discharges. These models predict that in atmospheric pressure energetic electrons driven by the discharge can establish and maintain electron-density nonequilibrium of over six orders of magnitude. An unexpected result is an “S-shaped” dependence of $n_e$ on $T_e$ at steady-state for a given gas temperature. This behavior results from a transition between predominately molecular ions to atomic ions at a critical value of $T_e$ and values of $n_e$ above about $10^{14}$cm$^{-3}$. Above this critical value of $T_e$, the electron density increases dramatically so that three-body recombination can maintain a steady state.

The feasibility of such nonequilibrium discharges was demonstrated in atmospheric-pressure air at around 2000K with electrode spacings of cm scale. Stable, diffuse DC discharges have been achieved at atmospheric pressure for a range of gas flow and temperature conditions including those which produce $n_e$ of $10^{12}$ to $10^{13}$cm$^{-3}$ without significant gas heating. Good agreement between theoretical and measured discharge characteristics has been obtained for air discharges over a wide range of conditions including electron densities greater than $10^{14}$cm$^{-3}$.

To reduce the power required to maintain such nonequilibrium, the finite electron recombination time (~10µs) has been exploited by means of pulsed discharges of 10ns duration. Both single-shot and repetitively pulsed diffuse discharges at 100kHz have been demonstrated, with power reductions of over two orders of magnitude for average electron densities greater than $10^{12}$cm$^{-3}$. Current experiments are exploring larger-scale discharges with multiple electrodes.

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