Chemical kinetic modelling of NO_x formation in Transient Spark discharge

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Transient Spark (TS) discharge generated in atmospheric air is an efficient source of NO_x for biomedical applications with a negligible O_3 production. The TS discharge is characteristic by short (~10-100 ns) and high current (~1-20 A) spark pulses initiated by streamer. The paper presents chemical kinetic model of the TS with focus on generation of selected reactive oxygen and nitrogen species (RONS), e.g. O, N, NO, NO_2, and O_3, that are important for their antibacterial and other biomedical effects. The dominant intermediate product of the streamer-induced chemistry is atomic O. The chemistry is twisted towards production of reactive nitrogen species in the spark phase, as the density of N atoms exceeds the atomic O density. However, the generation of NO_x occurs mainly during the relaxation phase following the TS pulse, which is not yet included in the present model.

1. Introduction

The Transient Spark (TS) is a dc-operated self-pulsing (~1-10 kHz) discharge initiated by a streamer [1]. Thanks to the short (~10-100 ns) high current (~1-20 A) spark pulses, the TS generates strongly ionized and highly reactive non-equilibrium plasma with the electron density above 10^{17} cm^{-3} [2]. The NO_x production rate ~7×10^{16} molecules/J was achieved [3]. We assume that further enhancement of NO_x formation by TS is possible. Finding appropriate conditions for even higher NO_x production rate requires further investigations of TS including kinetic modelling, to which this study is devoted.

2. Model description

The chemical kinetic modelling is commonly used in plasma chemistry. Our model is based on the existing ZDPlasKin module [4] and set of plasma chemical processes in N_2-O_2 mixtures provided by ZDPlasKin authors (version 1.03). The ZDplasKin package includes a Bolsig+ solver for the numerical solution of the Boltzmann equation. The electron scattering cross sections were taken from the LXCat project database [5]. The additional module compatible with ZDPlasKin was created, taking into account fast changes of conditions (reduced electric field strength *E/N*, gas temperature, etc.) during the evolution of TS discharge, starting from the primary streamer till the end of the spark phase.

More details on the simulation of TS streamer phase in our model can be found in Ref. [6]. The spark pulse in our model is induced by hydrodynamic expansion causing the decrease of gas density (*N*), increasing thus *E/N* and the electron temperature T_e. We used the *N* profile from the hydrodynamic model of Naidis [7].

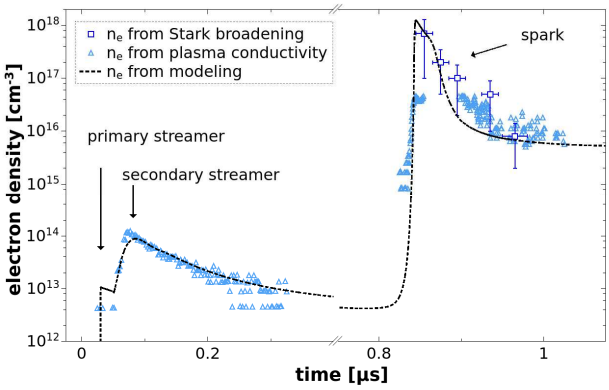

Fig. 1. Comparison of the measured and calculated electron density.

During the spark phase characterized by a high degree of ionization and atomization, the model uses Maxwellian electron energy distribution functions defined by the T_e. The temporal evolution of T_e during the spark phase is calculated by the energy balance equation.

The duration of the spark phase in our model is 400 ns. As we found, it is long enough for plasma to become weakly ionized again. Next, we assume that it is short enough to neglect processes such as diffusion or mixing with the surrounding air during this phase. These processes will be included in the following relaxation phase of the TS discharge, which is not included in the present model yet.

3. Results and discussion

The present model reasonably calculates the electron density n_e evolution that is in a good agreement (Fig. 1) with experimental data [3]. We thus assume that this model can be used to determine

reliably the density evolution of other species included in it. Here we focus on temporal evolution of the selected RONS: NO, NO_2, N, O, and O_3.

Each TS spark pulse is initiated by the primary streamer with strong electric field in its head, where the electrons gain high energy and are able to initiate various chemical processes. During the secondary streamer phase, the field is lower, but the duration of the secondary streamer is longer and therefore higher n_e is achieved (Fig. 1). For this reason, the secondary streamer strongly influences the density of produced RONS [6]. Later, during the streamer-to-spark transition phase, the changes of selected RONS densities are relatively slow.

The density of atomic O is the highest among the RONS after the secondary streamer. When we simulated a hypothetical case with primary and secondary streamer but no spark [6], the final dominant product was O_3.

The spark phase is characterized by a strong increase of the ionization degree, gas temperature and dissociation of molecules. The molar fraction of NO decreases by three orders of magnitude during the initial part of the spark phase. The dissociation degree of three-atomic molecules (NO_2, O_3) is even higher, approximately by two orders of magnitude. Thus, we can conclude that NO, NO_2 and O_3 densities achieved before the spark have almost no influence on the final densities of these species.

Their final densities will be established later during the relaxation phase, which is not included in the model yet. During the spark phase, we mostly see generation of their precursors: N and O atoms. Unlike in the previous phases, the amount of N exceeds the amount of O atoms during the spark phase (Fig. 2). This is the first indicator of the experimentally observed result that TS generates significantly more NO_x than O_3 [3].

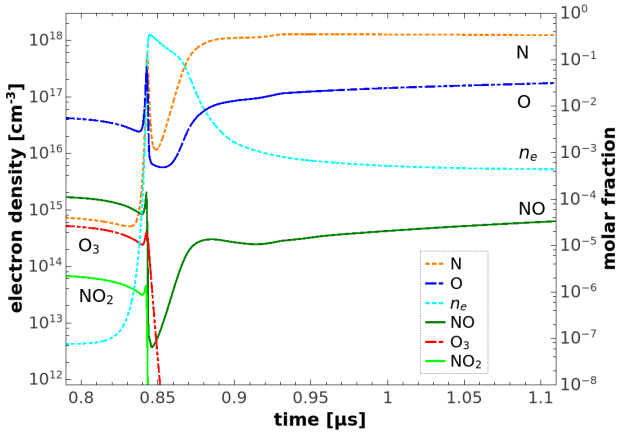

Fig. 2. Calculated electron density and molar fraction of selected RONS during the spark phase.

4. Conclusions

The 0-D model based on ZDPlasKin module was successfully used to model plasma induced chemistry during the transient events propagating in space, such as primary and secondary streamers. The ZDPlasKin was also used to model plasma chemistry during the spark phase of the transient spark discharge characterized by highly ionized non-thermal plasma. The electron density calculated in the model agrees well with experimental observations.

We further focused on the production of selected RONS playing important roles in biomedical applications of electrical discharges in air: O, N, NO, NO_2 and O_3. In transient spark, the experimental data shows that NO_x are dominant products and the amount of generated O_3 is negligible. Our model indicates that this results from the enhancement of atomic N generation and gas heating during the spark phase. Calculated density of N atoms exceeds the density of O atoms during the spark phase.

Due to the strong degree of atomization during the spark phase, the production of stable products NO, NO_2 and O_3 determining their final densities must occur later, during the TS relaxation phase. We plan further development of our kinetic model to be able to reliably simulate the relaxation phase of the TS discharge to prove this hypothesis and find better correlation with experiments.

Acknowledgement

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