Modeling of chemical reactions in an atmospheric pressure plasma: towards an estimation of O, N, and OH radical production

A. Komuro[1], R. Ono[1], T. Oda[2]

[1] *Department of Advanced Energy, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba, 227-8568, Japan*

[2]*Department of Electrical Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan*

Introduction

Non thermal plasma generated in an atmospheric pressure air has attracted great interest because of its non thermal property and high reactivity [1]. The streamer discharge (e.g. corona discharge and dielectric barrier discharge) is one of these non thermal plasmas. In the streamer discharge, chemically active species such as O, N and OH are produced and play important roles in many applications. However, the understanding of radical production in the streamer discharge is still poor. The applications need to be optimized in a very scientific way to both improve the energy efficiency and confirm the safety of the technologies.

Simulation model

The production process of O, N, and OH radicals in an atmospheric-pressure streamer discharge is studied. A streamer discharge model is developed to analyze the characteristics of a pulsed positive streamer discharge in point-to-plane electrodes filled with humid air at atmospheric pressure. To compute the propagation of a streamer in air, we use the first-order electro-hydrodynamic model for electrons and positive and negative ions in the framework of the drift-diffusion approximation. Thus, the equations involved in this model are as follows:

$$\frac{\partial n_s}{\partial t} + \mathrm{div}(n_s v_s(E/N)) = S_s(E/N), \quad s = e,p,n \tag{1}$$

$$n_e v_e(E/N) = n_e \mu_e(E/N)E - D_e(E/N)\mathrm{grad}(n_e), \tag{2}$$

$$n_p v_p(E/N) = n_p \mu_p(E/N)E, \tag{3}$$

$$n_n v_n(E/N) = n_n \mu_n(E/N)E, \tag{4}$$

$$\mathrm{div}E = \frac{e}{\varepsilon_0}(n_p - n_e - n_n), \tag{5}$$

where n_s, $v_s(E/N)$, $S_s(E/N)$, $\mu_s(E/N)$, and $D_s(E/N)$ are the charged particle density, charged particle velocity, particle chemical source term, mobility, and diffusion coefficient, respectively.

The subscript “s” denotes electrons (e) or positive (p) or negative (n) ions. E is the electric field, ε_0 is the permittivity of free space, and e is the absolute value of the electronic charge. The transport and source parameters involving electrons (such as v_e, D_e, and the reaction coefficients in S_s) are calculated using Bolsig+ [2] with published e-V cross sections [3]. We used a reduced reaction model including electron impact reactions (excitation, ionization, dissociation, re-combination, attachment and detachment), ion recombi-nation and the reactions of neutrals. A detailed description of the chemical reaction model is given in our previous paper [6]. In the charged-particle kinetics, three positive ions: N_2^+, O_2^+, and H_2O^+, four negative ions: O_2^-, O^-, OH^-, and H^-, and electrons are considered. Complex ions such as O_4^+, N_4^+, and $O_2^+N_2$ and the charge transfer reactions are not considered in this simulation. The charged species transport equation (1) is solved using the MUSCL superbee algorithm [4]. In (3) and (4), all ion mobilities are assumed to be 2.2×10^{-4} $m^2V^{-1}s^{-1}$ [5] and diffusion is neglected for the ionic species. It is assumed that neutral molecules are stationary throughout the entire field.

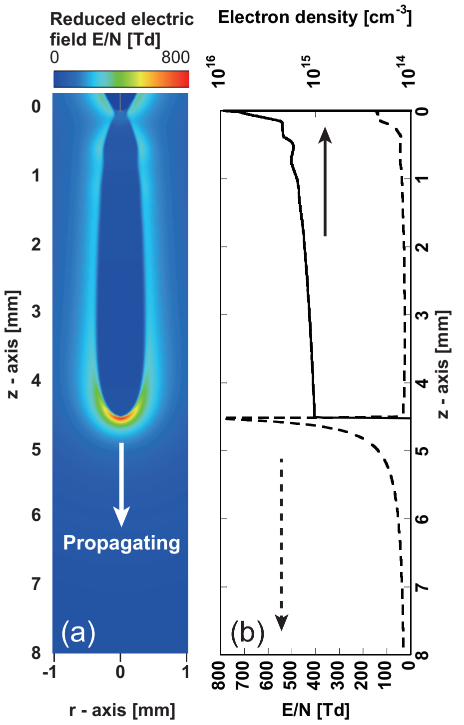

Figure 1: (a) Cross sectional views of reduced electric field and (b) the axial distribution of reduced electric field (in Td) and electron density (in cm^3) for 13 mm gap discharge.

Results

Discharge kinetics

Figure 1 shows calculated two-dimensional structures of the absolute value of the reduced electric field (E/N) and the axial distributions of E/N and the electron density. The distance from the anode tip in the direction of the plane cathode is defined as z and that from the central axis is defined as r, corresponding to our experimental configuration. Figure 1 indicates that the streamer head propagates with a high electric field toward the cathode and that the streamer channel acts as a highly conductive channel connecting the streamer head to the anode. The reduced electric field is 20 Td in the streamer channel and approximately 800 Td at the streamer head. Figure 1(b) shows that the electron density in the streamer channel is higher than 10^{15} cm^{-3}.

O radical production

Figure 2 (a) shows the axial distributions of streamer luminous intensity for V = 32, 24, 16 kV.

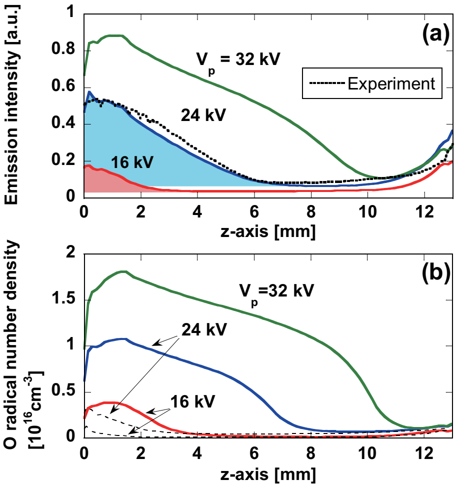

Figure 2: Axial distributions of (a) streamer luminous intensity and (b) oxygen radical density at 200 ns for the voltage V = 32, 24, 16 kV in O_2(20%)/N_2.

The shaded are-as in figure 2 (a) represent the luminescence from the secondary streamer and the unshaded areas represent that from the primary streamer [7]. The broken line shows our experimental data obtained from a streamer discharge reactor with 25 gaps under the same conditions [8]. In the 25-gap reactor, monofilament streamers are generated, similar to those appearing under our simulation conditions. The ratios between the emission intensities from the primary and secondary streamers in figure 2 (a) obtained experimentally and by simulation at V = 24 kV are in good agreement. Figure 2 (b) shows axial distributions of O radical density at t = 200 ns for V = 32, 24, and 16 kV. The axial distributions of streamer luminous intensity in figure 2 (a) and those of oxygen radical density are in reasonably good agreement. This agreement has already been observed in our experimental results [9]. In our simulation, O radicals are mainly produced by both the electron impact dissociation process and the dissociation of O_2 by the excited nitrogen molecules $N_2(B'^3\Sigma_u^-, C^3\Pi_u)$.

N radical production

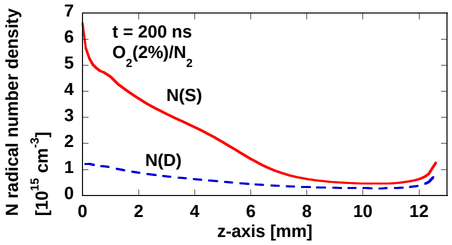

Figure 3: Axial distributions of nitrogen radical densities at $t = 200$ ns in O_2(2%)/N_2.

Our previous experimental measurement shows that nitrogen radicals are mainly produced in the secondary streamer region in O2(2%)/N_2 [10]. Although we could not give a clear explanation for the high dissociation degree of N_2 in the secondary streamer, the experimental result that the production yield of nitrogen radicals is approximately proportional to the square of the discharge energy strongly indicated the contribution of two-step dissociation reactions [10]. The following reactions have been proposed as a source of dissociation:

$$\mathrm{R1:}\quad \mathrm{N_2 + e \rightarrow N(^4S) + N(^2D) + e}$$

$$\mathrm{R2:}\quad \begin{cases} \mathrm{N_2 + e \rightarrow N_2}(v) + \mathrm{e} \\ \mathrm{N_2}(v) + \mathrm{e \rightarrow N(^4S) + N(^4S) + e} \end{cases}$$

Figure 3 shows the simulated axial distributions of the N(^{4}S) and N(^{2}D) radical densities at t=200 ns in an O_2(2%)/N_2 mixture. The excited N(^{2}D) radicals are produced by the direct dissociation reaction R6. The discrepancy between the axial distributions of N(^{4}S) and N(^{2}D) shows the contribution of the two step dissociation reaction R6 to the production of N(^{4}S) radicals. This result indicates that while reaction R6 is more prevalent than reaction R6 in the primary streamer, reaction R6 is more prevalent than reaction R6 in the secondary streamer and that most of the N(^{4}S) radicals are produced by reaction R6.

OH radical production

The number of OH radicals produced in a single discharge pulse is simulated as shown in figure 4. Then, the effect of the humidity on the number of OH radicals generated is compared with the experimental results [11]. Figure 4 indicates that the number of OH radicals produced by the discharge is saturated with increasing water vapor, and the simulation result is qualitatively consistent with the experiments except for a difference in the total number of OH radicals within a factor of 2. Let me ex-plain the mechanism of OH radical production and loss processes. The OH radicals are mainly produced in the secondary streamer, and the dissociation of H_2O by O(^{1}D) and N_2(a) is predominant in the production of OH. After the production of OH radicals, the OH radical density is rapidly decreased by the reactions of OH with O(^{3}P). However, the H radicals resulting from the OH + O(^{3}P) and OH + N(^{4}S) reactions are transformed into HO_2, then the HO_2 produces OH again by the reaction with O(^{3}P). Once the above“ OH-cycle ”reactions reach quasi-equilibrium, the “ OH-recombination ”reaction comes into play. As a result, the produced OH change into H_2O or H_2O_2 by recombination reactions with water-related radicals. This is the reason why the OH radicals produced are saturated with water vapor as shown in figure 4.

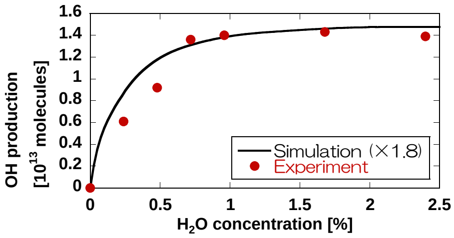

Figure 4: Total number of OH radicals at t = 3 μs as a function of H_2O concentration. Experimental values were measured in our previous work [11].

References

[1] Seiji Samukawa *et al.* 2012 *J. Phys. D.* **45** 253001.
[2] Hagelaar G J M and Pitchford L C 2005 *Plasma Sources Sci. Technol.* **14** 722-33.
[3] PHELPS database, http://www.lxcat.laplace.univ-tlse.fr, retrieved March 11, 2011.
[4] Ferziger J H and Perić M 1996 Computational Methods for Fluid Dynamics (Springer).
[5] Tochikubo F and Arai H 2002 *Jpn. J. Appl. Phys.* **41** 844-52.
[6] Komuro A, Ono R and Oda T 2013 *J. Phys. D : Appl. Phys.* **46** 175206.
[7] Ono R and Oda T 2003 *J. Phys. D: Appl. Phys.* **36** 1952-58.
[8] Ono R, Nakagawa Y and Oda T 2011 *J. Phys. D: Appl. Phys* **44** 485201.
[9] Ono R, Takezawa K and Oda T 2009 *J. Appl. Phys.* **106** 043302.
[10] Teramoto Y, Ono R and Oda T 2012 *J. Appl. Phys.* **111**, 113302.
[11] Nakagawa Y, Ono R and Oda T 2011 *J. Appl. Phys.* **110** 073304.