Characterization of OH species in atmospheric-pressure air dielectric-barrier discharges

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Abstract: This work conducts both experiments and numerical simulations to investigate the OH species generated in APADBDs at different H₂O concentrations. The APADBDs are generated by a kHz power supply with humid air and simulated by the integration of the 1.5D plasma fluid model and 3D gas flow model. The preliminary results show that the measured OH density is around 1.0×10^{19} m⁻³ in the case with 1.6 % H₂O concentration, which agrees with that simulated. The simulated results are presented and discussed.

Keywords: DBD, air, OH, atmosphere, kHz, UVAS.

1. Introduction

Atmospheric-pressure air dielectric barrier discharges (APADBDs) have been developed for decades due to the high economic benefit of the generation of abundant reactive species. The OH molecules generated within the APADBDs play important roles in applications including pollution control of volatile organic compounds [1-2] and plasma-assisted combustion [3-4]. To have a better understanding of OH species, it is essential to realize the production and consumption mechanisms within APADBDs. Therefore, this work conducts both experiments and numerical simulations to investigate the OH species generated in APADBDs at different H₂O concentrations. The APADBDs are generated by a kHz sinewave power supply, and OH densities are measured for cases with different H₂O concentrations by ultraviolet absorption spectroscopy (UVAS) [5]. The average OH molecules generated by a single microdischarge (MD) are modeled by the 1.5D plasma fluid model (PFM) and integrated with a 3D gas flow model (GFM) to simulate the OH density generated in the reactive zone [6-7]. The average spatial-cyclic species sources generated in a single MD are calculated in the 1.5D PFM by considering the discharge dynamics with the heating sources including elastic collisions, ionic joule heating, and inelastic collisions calculated. The proposed concept of equivalent reaction is implemented to evaluate the equivalent amounts of reactive species generated by MDs in the reactive zone in the 3D GFM with the effect of gas heating. The equivalent reactions in the 3D GFM are implemented to mimic the complex environment beyond MDs in the reactive zone with some essential reactive species including OH, H, and H₂O₂ considered since these species are highly related to the OH generation and destruction mechanisms. The simulated results are compared with experimental measurements to validate the model. After the model validation, detailed generation and destruction mechanisms are analyzed and presented.

2. Experimental methodology

Fig. 1 shows the schematic diagram of the experimental measurements. A planer reactor with indium tin oxide coated on one side of the glass plates as the transparent electrodes is designed for generating APADBDs. The gap distance between the dielectrics is 1.4 mm. The dimensions

of the reactive area are 40 mm \times 7.5 mm located in the central region of the glass plate. The sidewalls of the reactor, which are fabricated by quartz plates, are used for conducting measurements of the UVAS. A kHz sinewave power supply (Nai-Ding, PP-50501-AVF) is used with the voltage and frequency controlled at 6.8 ± 0.1 kV and 16.5 \pm 0.1 kHz, respectively. The voltage and current are measured by the high-voltage probe (Tektronix, P6015A) and current probe (Tektronix, CT-1) respectively. The digital oscilloscope (Keysight, DSOX3054T, 500 MHz, and 5.0 GSa/s) is used to store the discharge electrical behavior and evaluate the power consumption by using the Lissajous curve. The working gas from the air bottle is divided into dry airflow and the other airflow with saturated water vapor. Both flow rates are controlled by the flow meters. The total gas flow rate supplied from the top of the reactor is controlled at 1 SLM. The temperature distribution of the reactor surface is measured by an infrared (IR) thermal imager (AVIO, F50A) for validating the correctness of the model. Fig. 2 shows the schematic diagram of the UVAS for measuring the OH densities at the middle region of the reactive area. The UV light emitted from a LED (Mightex, LCS-0310-03-23) light source passes through the reactive area and is collected by the optical fiber connected to the spectrometer (Avantes, AvaSpec-ULS4096CL-EVO). A pinhole is set between the reactor and the optical fiber to avoid stray light. According to Beer-Lambert's law, the OH density is evaluated from the measured light intensity, written as

OD
$$(\tilde{\upsilon}) = \ln\left(\frac{l_0(\tilde{\upsilon})}{l(\tilde{\upsilon})}\right) = \sigma_{\text{eff}}(\tilde{\upsilon}) \times l \times [OH]$$
 (1)

$$\sigma_{eff}^{ij}(\tilde{v}) = n_i \, \sigma^{ij}(\tilde{v}) = n_i \, \sigma_{tot}^{ij} \, F(\tilde{v}) \tag{2}$$

where $I_0(\tilde{v})$ is the light intensity measured without the discharge, $I(\tilde{v})$ is the light intensity measured with the discharge, σ_{eff} is the absorption cross-section of OH, 1 is the absorption length, [OH] is the OH density, $\sigma_{eff}^{ij}(\tilde{v})$ is the effective absorption cross-section, and n_i is the fractional population of OH molecules in the transition originating from the lower states *i*. The average OH densities measured along the optical path are compared with the simulated average OH densities to validate the developed model.

3. Numerical methodology

The previously developed 1.5D PFM is used to capture the momentary dynamics of a single MD generated in the APADBDs [8]. A single MD is modeled in the 1.5D PFM to simulate the average MD properties since it was reported that MDs have similar properties as the numerical domain shown in Fig. 3 under the uniform assumption with a single MD [9]. The average MD radius and dimension of the surface wave are assumed as those measured in [9]. The Poisson equation and the photoionization effect are solved in the 2D axisymmetric domain to capture the intensive electric field in front of the streamer wavefront, while the continuity equations of species and electron energy density equation are solved in the 1D domain to save the runtime. In the 1.5D PFM, the electron dynamics is considered by solving the continuity equation with the source term calculated from the discharge chemistry. The externally applied voltage is implemented as the boundary condition of the Poisson equation to calculate the potential distribution for evaluating the local electric field within the gap. The spatial-cyclic average species sources and heating source are calculated and provided as the input parameters in the 3D GFM as introduced next.

The 3D GFM is developed to model the steady-state distributions of reactive species in the reactive zone with the effect of gas temperature considered. Fig. 4 shows the numerical domain of the 3D GFM. Only a quarter of the reactor is built due to the symmetric structure. The airflow is supplied from the top of the reactor and leaves from the outlet at the bottom of the reactor. The dimensions of the reactive zone are identical to those of the reactor designed for experiments. The commercial software CFD-ACE+ is applied to build the 3D GFM. The flow dynamics of background gases is modeled by solving the flow continuity and momentum equations. The total enthalpy equation is solved to model the temperature distribution of the reactor with the heating source obtained from the 1.5D PFM. The simulated gas temperature in the 3D GFM is used as the background gas temperature in the 1.5D PFM to model the average properties of a single MD for calculating the spatial-cyclic average species source of each reactive species considered. A few iterations between the 1.5D PFM and 3D GFM are required to obtain converged solutions. The chemical model in Table 1 is considered in the 3D GFM to evaluate the source term of each species considered in the 3D GFM for modeling the distribution of reactive species in the reactive zone. Some essential reactive species including OH, H, and H₂O₂ are considered since these species are highly related to the OH destruction mechanisms. generation and The computational domain of the reactor is surrounded by ambient air used to model the cooling effect caused by natural convection.

To integrate the reactive species generated in the 1.5D PFM to the 3D GFM, the spatial-cyclic average species source of each reactive species considered in the 3D GFM is calculated as the equivalent rate constant and provided as the source term of the chemical model considered in

Table 1 in the 3D GFM. The equivalent rate constants of the corresponding equivalent reactions (R1-R3) in the 3D GFM are used to model the species densities in the reactive zone. The production rate of each equivalent reaction is used to generate the same amount of reactive species generated by MDs in the reactive zone of the 3D GFM as that of OH species written as

$$PR_{OH} = 4 \times ERC_{OH}[0_2][H_20][H_20]\frac{\text{kmole}}{\text{m}^3 \cdot \text{s}} \quad (3)$$

where PR_{OH} is the production rate of OH, $[O_2]$ is the density of O_2 , and the equivalent rate constant (ERC_{OH}) can be written as

$$ERC_{OH} = \frac{SS_{OH} \times Vol_{MD} \times N_{MD}}{4 \times Vol_{RZ} \times [O_2] \times [H_2 O] \times [H_2 O]}$$
(4)

where SS_{OH} is the average volumetric species source calculated by the 1.5D PFM, Vol_{MD} is the average volume of a single MD, N_{MD} is the number of MDs, Vol_{RZ} is the volume of the reactive zone.

4. Results and discussion

After the temperature of the reactor surface reached the steady state, the preliminary average OH density measured at the central region of the reactive zone reaches 1.0×10^{19} m⁻³ in case with 1.6 % H₂O concentrations. The preliminary result shows that the simulated OH density reaches around $7.8 \times 10^{18} \,\mathrm{m}^{-3}$, agreeing with that measured. It is noted that the simulated density is evaluated from the average density along the optical path in the 3D GFM. The preliminary analysis shows that electron-impact dissociation ($e + H_2O \rightarrow e + OH + H$) and electron-ion ($e + H_2O \rightarrow e + OH + H$) $H_2O^+ \rightarrow OH + H$) recombination reactions contribute to over 80 % of the OH generation. The interactions among OH species and other reactive species including NO_x (e.g., NO, NO₂, and NO₃) and O₃ are ongoing for having a better understanding of the discharge chemistry. The compiled measured and simulated average OH densities in cases with different H₂O concentrations will be presented with the improved chemistry model.

5. Conclusion

This work conducts both the experimental measurements and the numerical simulations to investigate the OH species generated in atmospheric-pressure air dielectric barrier discharges at different H₂O concentrations. The previously developed 1.5D PFM is used to capture the momentary dynamics of a single MD generated in the APADBDs in conjunction with the 3D GFM to simulate the OH molecules generated by MDs in the reactive zone. The preliminary results show that the measured OH density is around 1.0×10^{19} m⁻³ in the case with 1.6 % H₂O concentration, which agrees with that simulated to validate the model developed. The preliminary analysis shows that electron-impact dissociation and electron-ion recombination reactions contribute to over 80 % of the OH generation. More interactions of reactive species will be

added to complete the chemical model. Further analysis details will be presented and discussed onsite in the conference.

6. References

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Fig. 1. Schematic diagram of the experimental measurements.



Fig. 2. Schematic diagram of the UVAS.



Fig. 3. Numerical domain of the 1.5D PFM.



Fig. 4. Numerical domain of the 3D GFM.

Table 1. Chemistry considered in the 3D GFM.

No.	Reaction	Rate constant
R1	$O_2 + 2 H_2O => 4 OH$	Equivalent reaction
R2	$2 H_2 O => 4 H + O_2$	Equivalent reaction
R3	$2 H_2O + O_2 \Longrightarrow 2 H_2O_2$	Equivalent reaction
R4	$2 \text{ OH} \Longrightarrow O + H_2O$	$5.3 \ge 10^3 \times \exp{(\frac{-503}{T_g})}$
R5	$OH + H + N_2 => N_2 + H_2O$	$5.42 \times 10^3 \times T_g^{-2}$
R6	$2 \ OH + N_2 \Longrightarrow H_2O_2 + N_2$	$1.21 \mathrm{x} 10^7 \times T_g^{-3.2}$
R7	$2\;H+N_2 => H_2 + N_2$	$2.21 \times T_{g}^{-1}$
R8	$H + H_2O_2 \Longrightarrow OH + H_2O$	$1.02 \ge 10^4 \times \exp{(\frac{-1800}{T_g})}$
R9	$H + H_2O_2 => H_2 + HO_2$	$1.69 \ge 10^3 \times \exp{(\frac{-1900}{T_g})}$
R10	$OH + H_2O_2 \Longrightarrow HO_2 + H_2O$	$1.75 \text{ x } 10^3 \times \exp{(\frac{-160}{T_g})}$
Note:		

1. Two-body reactions have units of m3 kmol-1 s-1

2. Three-body reactions have units of $m^6\,kmol^{-2}\,s^{-1}$

3. T_g is in the unit of K