MODELING THE PLASMA CHEMISTRY OF A PULSED CORONA DISCHARGE IN DRY AND HUMID AIR

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Abstract

We discuss kinetic modeling of the plasma chemistry of short pulse electrical discharges in mixtures of N_2, O_2, and H_2O at atmospheric pressure. Species such as O, OH, O_3, and NO_x, which are produced in these corona discharges, have important implications in the surface treatment of polymers.

Introduction

The very inert surfaces of polyolefins such as polypropylene and polyethylene, along with their low surface free energies, make printing on or adhering to them very difficult. As a result, these materials have to be surface treated before printing. Surface treatments transform the surfaces of polyolefin materials into more workable substrates. There is a growing interest in the use of plasmas to modify the surface structure and composition of these organic films. The ability of plasmas to produce unique surface modifications and the ease with which the extent of modification can be controlled, has given the plasma treatment process an advantage over other conventional processes such as mechanical abrasion, chemical etching, and flame treatment.

Plasma treatment involves a process whereby the polymer surface is subjected to a strong electric field in an ionized atmosphere, typically in air. A plasma produced by a corona discharge is the most commonly used surface treatment method in the plastic and film industry. In the process, highly oxidative molecules are formed. These strong oxidizing agents, for example atomic oxygen and free radicals such as OH, are then available to react with the surface. The nonpolar carbon-carbon bonds can subsequently be transformed into short-chain free radicals, which easily become oxidized, resulting in polar functional groups. This surface modification, which is confined to a very thin layer, typically 1-10 μm in depth, results in

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enhanced adhesion to other polar coating materials such as inks, adhesives, *etc.* The principal changes believed affected by exposure of a polymer to a corona discharge plasma are in the surface wettability, the molecular weight of the surface layer, and the chemical composition of the surface.

The goal of this work has been to understand the formation chemistry of radicals, which play a major role in the polymer surface chemistry, in order to provide guidance in optimizing discharge parameters and gas mixtures for surface treatment. It is most desirable to enhance the production of O and OH and minimize the production of deleterious radicals such as O_3 and NO_x.

Plasma Chemistry Modeling

We have modeled the time dependent non-equilibrium plasma chemistry of a pulsed DC discharge in N_2, O_2, and H_2O mixtures at atmospheric pressure. The use of short DC pulses, typically gaussian with a half width of 75-100 ns, allows the use of electric fields on the order of or even greater than the DC breakdown field, *i.e.* E/N$\simeq$160 Td (where 1 Td = 10^{-17} V-cm^2) without gas breakdown. In this modeling we have used the general non-equilibrium, time dependent plasma chemistry code, *KINEMA* [1], coupled with the electron Boltzmann equation solver, *ELENDIF* [1,2], and an air plasma chemistry model comprising more than 50 species and 300 reactions. As we have nearly 40 years of published research in the plasma chemistry of air to draw upon (see Ref. 3, for example), a model of this size is not unreasonable. This modeling was performed in conjunction with an experimental program [4]. The discharge parameters chosen here closely match those of the experiments.

That a solution of Boltzmann's equation for the electrons is necessary in this kind of modeling has been well established over the past 30 years. The energy loss by electrons exciting the low energy molecular vibrational modes and electronic states causes an excess of electrons in the distribution function at low energies (below 3 or 4 eV in air) and a resulting depletion of electrons in the tail of the distribution, which is responsible for ionization. Hence the ionization rate coefficients may be orders of magnitude smaller than would be predicted using a Maxwell-Boltzmann distribution of the same mean energy. A form of Boltzmann's equation formulated for electrons in a partially ionized gas is numerically solved [2] for the non-equilibrium electron energy distribution function from which we compute the electron impact rate coefficients for excitation and ionization of the major species in the plasma.

The electron impact processes, which drive the entire plasma chemistry in an electric discharge, comprise the following processes:

N_2	$\rightarrow$	$N_2(v)$, $N_2(A^3\Sigma)$, $N_2(a^1\Pi)$, N_2^*, N_2^+
O_2	$\rightarrow$	$O_2(v)$, $O_2(a^1\Delta)$, $O_2(b^1\Sigma)$, O+O, O_2^*, O_2^+
H_2O	$\rightarrow$	H+OH, H_2+O(^{1}D), OH^-+H, H^-+OH, O^-+H_2, H_2O^+
$N_2(A^3\Sigma)$, $N_2(a^1\Pi)$	$\rightarrow$	N_2^+
$O_2(a^1\Delta)$, $O_2(b^1\Sigma)$	$\rightarrow$	O_2^+
O	$\rightarrow$	O(^{1}D), O(^{1}S), O^+

Sources for these cross sections include References [5]-[8].

The air chemistry model consists of electron impact cross sections for excitation and/or ionization, electron-ion recombination, ion-molecule reactions, neutral and excited state chemistry, and ion-ion neutralization or recombination reactions. General compilations offering data for the other kinetic processes include References [9,10] (electron-ion recombination), [11,12] (ion-molecule reactions), [3,13] (N_2/O_2 plasma chemistry), and [14] (neutral chemistry). A wealth of information and data on negative ions can be found in Smirnov's book [15]. We will discuss particular aspects of the plasma chemistry as we describe the results of our calculations.

Calculations on Dry Air

We have performed calculations using Gaussian pulses for E/N(t) having a peak at 100 ns and values of the full width at half maximum of 75-100 ns. The peak values of E/N ranged from 150 Td to a maximum of about 200 Td..

The first series of calculations was performed for dry air, 79% N_2 and 21% O_2, at atmospheric pressure. Although the set of reactions consists of some 30 atomic and molecular species and 130 reactions the most important chemical pathways are:

$$
\begin{aligned}
e + O_2 &\rightarrow O^-, O, O_2^+ \\
O^- &\rightarrow O_2^- \rightarrow O_3^- \\
O^- &\rightarrow N_2O \\
O &\rightarrow O_3, NO \\
O_2^+ &\rightarrow O_4^+
\end{aligned}
$$

At long times the dominant ions are O_4^+ and O_3^-, which recombine, via the tidal recombination process [16] in the presence of an atmospheric pressure ambient gas, with a rate coefficient in excess of 10^{-6} cm^3/s. At lower values of E/N or reduced O_2 partial pressure the dominant ions may be NO^+ and NO_3^-.

A characteristic of electric discharges in oxygen is the formation of copious quantities of $O_2(a^1\Delta)$, which has a very small reactivity with most molecules. Of the species in this chemistry it reacts most strongly with O_3, NO, O(^{1}S), and O_4^+ with rate coefficients ranging from 10^{-11} to 10^{-10} cm^3/s. Due to the strong propensity

of molecular oxygen to predissociate, discharges in oxygen are also characterized by large quantities of atomic oxygen, which invariably leads over time to large amounts of ozone.

Although the finest quantitative details of this modeling may be uncertain we expect the trends that we predict from the calculations to be valid. From examining the results of varying E/N, pulse length, and O_2 partial pressure we have drawn the following conclusions:

(1) reducing the pulse length allows the use of a greater peak value of E/N, which results in a greater fraction of the discharge power going into the dissociation of O_2 and formation of atomic oxygen;

(2) reducing the partial pressure of O_2 results in a greater mean electron energy and electron density for a given E/N and, consequently, a greater efficiency for the formation of atomic oxygen; thus there should exist some optimum pressure for maximum efficiency of formation of atomic oxygen; an added benefit is that the time scale for formation of ozone is increased; finally, as stated above, the dominant ions become NO^+ and NO_3^-.

A Comment on Gas Breakdown

An observation arising out of this modeling is the following sequence of events, considering only the plasma chemistry and not spacial effects, streamer formation, *etc.*, leading to gas breakdown at a fixed value of E/N:

(1) dissociation of molecular species, resulting in an increased electron mean energy for a given E/N;

(2) excitation of substantial populations of atomic metastables;

(3) stepwise ionization of excited atomic states leading to increased electron density for a given E/N; in addition, atomic ions can only recombine via termolecular collisional radiative recombination, which is generally much less rapid than the dissociative recombination that most molecules undergo;

(4) at a high enough electron density electron-electron collisions thermalize the electron energy distribution raising its tail and further increasing the ionization rate.

From a plasma chemistry perspective breakdown always goes through the same sequence of steps but occurs on shorter and shorter time scales as E/N is increased. Published breakdown curves are based on measurements made on macroscopic time scales (see Cobine, Ref. 17). Under short pulse conditions values of the breakdown E/N can be exceeded for a given set of external conditions (*i.e.*, pressure, temperature, gap length, electron geometry, *etc.*).

Calculations on Humid Air

We have performed calculations, similar to those for dry air, on mixtures of N_2, O_2, and H_2O. It is well known that water has a profound effect on electric discharges. The ionic character of the plasma becomes completely different at

humidity levels of only a per cent or two.

All the positive ions present in the dry air plasma either charge transfer to H_2O or form H_3O^+ via termolecular collisions with rate coefficients ranging from gas kinetic to 100 times gas kinetic. All negative ions of oxygen and nitrogen form negative cluster ions in termolecular collisions with water and the ambient molecular gas with rate coefficients that range from 10 to 100 times gas kinetic [11]. Hence the typical ionic composition of a humid air plasma will comprise H_3O^+, $O_x^-\cdot(H_2O)_n$, and $NO_x^-\cdot(H_2O)_n$, where n is typically equal to 2 or 3 at atmospheric pressure. The negative ions typically have rate coefficients for dissociative recombination with electrons of several times 10^6 cm^3/s at 300K [10]. The rate coefficients for recombination of the positive and negative cluster ions is also, as mentioned above, several times 10^6 cm^3/s [16].

The presence of water vapor has a small effect on the electron energy distribution function that amounts to a several per cent reduction in the mean electron energy at these high values of E/N. This reduces ionization rate coefficients somewhat. The copious production of negative ions has a much greater effect on the electron density. At a given value of E/N, the electron density peaks at a smaller value and has a much more narrow pulse in time, due to negative ion formation, in humid air as compared to dry air. Consequently, one must increase the electric field if one wants a discharge with an electron density equivalent to that obtained in a discharge in dry air. This is a highly non-linear effect in that (a) it increases the mean energy and reaction rates, (b) the power into the plasma from the electric field is approximately proportional to $(E/N)^2$, and (c) the integral of the driving pulse,*i.e.* the total electrical energy into the plasma, is a complicated function of the peak value of E/N and the humidity level. This last comes about because there is a threshold value of E/N, which we compute, for example, to be 157 Td for 50% humidity, below which the attachment rate coefficient, k_a, is greater than the ionization rate coefficient, k_i. Since only values of E/N greater than a humidity dependent threshold defined by $k_i \geq k_a$ can drive the discharge, the integrated power into the plasma is a function of humidity level even for fixed E/N.

The primary neutral product resulting from the presence of water vapor in a discharge is the hyroxyl radical, OH, which is produced abundantly by:

$$e + H_2O \rightarrow H + OH + e \text{ and } H^- + OH$$

which have a combined rate coefficient comparable with that for dissociation of O_2. As noted above, hydroxyl is a desirable product from the perspective of polymer surface treatment. On time scales of tens of microseconds the hydroxyl is converted to H_2O_2, HO_2, H_2O, and various HNO_x.

Clearly there are still many questions concerning the processes and products in the humid air plasma chemistry. The study of these discharges is continuing.

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[1] A product of *Kinema Research & Software;* for further information contact Kinema Research & Software or see the World Wide Web Home Page: "http://www.csn.net/~morgan".

[2] W.L. Morgan and B.M. Penetrante, *Comp. Phys. Comm.* **58**, 127 (1990).

[3] F.E. Niles, *J. Chem. Phys.* **52**, 408 (1970).

[4] J.E. Ansbro, *M.S. Thesis,* Dept. of Chemical Engineering, Michigan Technological University (1993).

[5] A.V. Phelps and L.C. Pitchford, JILA Information Center Report No. 26, University of Colorado (1985); *Phys. Rev. A* **31**, 2932 (1985).

[6] A.V. Phelps, JILA Information Center Report No. 28, University of Colorado (1985).

[7] M. Hayashi, in *Swarm Studies and Inelastic Electron-Molecule Collisions,* L.C. Pitchford, B.V. McKoy, A. Chutjian, and S. Trajmar, eds., Springer-Verlag, New York (1987), p. 101.

[8] I. Shimamura, *Scientific Papers of the Institute of Physical and Chemical Research* **82**, 1 (1989).

[9] J.B.A. Mitchell, *Physics Reports* **186**, 215 (1990).

[10] M.A. Biondi, in *Applied Atomic Collision Physics, Vol. 3,* E.W. McDaniel and W.L. Nighan, eds., Academic Press, New York (1982), p. 173.

[11] W.J. Wiegand, *ibid.*, p. 71.

[12] V.A. Anicich, *J. Phys. Chem. Ref. Data* **22**, 1469 (1993).

[13] I.A. Kossyi, A. Yu Kostinsky, A.A. Matveyev, and V.P. Silakov, *Plasma Sources Sci. Technol.* **1**, 207 (1992).

[14] W.G. Mallard, NIST Chemical Kinetics Database (1992).

[15] B.M. Smirnov, *Negative Ions,* McGraw-Hill, New York (1982).

[16] W.L. Morgan and D.R. Bates, J. *Phys. B* **25**, 5421 (1992).

[17] J.D. Cobine, *Gaseous Conductors,* Dover, New York (1958), Ch. 7.