Time-resolved electron temperature and electron density measurements in a nanosecond pulse filament discharge in \( \text{H}_2 \)--He and \( \text{O}_2 \)--He mixtures

A Roettgen, I Shkurenkov, M Simeni Simeni, I V Adamovich and W R Lempert

Department of Mechanical Engineering, Michael A Chaszeyka Nonequilibrium Thermodynamics Laboratories, The Ohio State University, Columbus, OH 43210, USA

E-mail: adamovich.1@osu.edu

Received 11 May 2016, revised 10 July 2016
Accepted for publication 26 July 2016
Published 16 August 2016

Abstract
Time evolution of electron density and electron temperature in a nanosecond pulse, diffuse filament electric discharge in \( \text{H}_2 \)--He and \( \text{O}_2 \)--He mixtures at a pressure of 100 Torr is studied by Thomson/pure rotational Raman scattering and kinetic modeling. The discharge is sustained between two spherical electrodes separated by a 1 cm gap and powered by high voltage pulses ~150 ns duration. Discharge energy coupled to the plasma filament ~2--3 mm in diameter is 4--5 mJ/pulse, with specific energy loading of up to ~0.3 eV/molecule. At all experimental conditions, a rapid initial rise of electron temperature and electron density during the discharge pulse is observed, followed by the decay in the afterglow, over ~100 ns--1 \( \mu \)s.

Electron density in the afterglow decays more rapidly as \( \text{H}_2 \) or \( \text{O}_2 \) fraction in the mixture is increased. In \( \text{He}/\text{H}_2 \) mixtures, this is likely due to more rapid recombination of electrons in collisions with \( \text{H}_3^+ \) and \( \text{H}_4^+ \) ions, compared to recombination with \( \text{He}_2^+ \) ions. In \( \text{O}_2/\text{He} \) mixtures, electron density decay in the afterglow is affected by recombination with \( \text{O}_2^+ \) and \( \text{O}_4^+ \) ions, while the effect of three-body attachment is relatively minor. Peak electron number densities and electron temperatures are \( n_e = (1.7--3.1) \times 10^{14} \text{ cm}^{-3} \) and \( T_e = 2.9--5.5 \text{ eV} \), depending on gas mixture composition. Electron temperature in the afterglow decays to approximately \( T_e \approx 0.3 \text{ eV} \), considerably higher compared to the gas temperature of \( T = 300--380 \text{ K} \), inferred from \( \text{O}_2 \) pure rotational Raman scattering spectra, due to superelastic collisions.

The experimental results in helium and \( \text{O}_2--\text{He} \) mixtures are compared with kinetic modeling predictions, showing good agreement.

Keywords: nanosecond pulse discharge, Thomson scattering, electron density, electron temperature, Raman scattering

(Some figures may appear in colour only in the online journal)

1. Introduction
The present work continues studies of electron kinetics in transient nonequilibrium high-pressure plasmas generated by high-voltage, nanosecond duration pulsed discharges. These discharges are routinely used in several rapidly developing applications, such as electric discharge pumped molecular lasers [1], plasma medicine [2], plasma assisted combustion [3], and plasma flow control [4]. However, time-resolved measurements of electron density and
electron temperature in ns pulse discharges and the afterglow are quite limited. These data are critical for quantitative insight into kinetics of ionization, recombination and attachment, ion–molecule reactions, charge accumulation on dielectric surfaces, ionization wave propagation, generation of metastable species and highly reactive radicals, and validation of kinetic models. The objective of the present work is to quantify the effect of adding hydrogen and oxygen to the baseline helium flow on electron density and electron temperature in a nanosecond pulse discharge and the afterglow, using Thomson scattering. The principal motivation for studying electron kinetics in H2–He mixtures is low-temperature plasma assisted combustion, for which ns pulse discharges have been used extensively. Plasma jets generated by ns discharge pulses in O2–He mixtures are increasingly widely used in biology and medicine for generation of reactive oxygen species. Specifically, measurements and prediction of electron density and electron temperature in these plasmas provide insight into partition of energy coupled to the plasma among different electron impact processes, including hydrogen and oxygen dissociation and electronic excitation of helium. In the present work, we use a volumetric ‘diffuse filament’ discharge sustained between two spherical electrodes, which is highly reproducible shot-to-shot, provides ample optical access, and allows time-resolved measurements of electron density, electron temperature, and gas temperature at high pressures (up to ~1 atm) and high specific energy loadings (up to ~0.5 eV/molecule). Specifically, this type of discharge lends itself to laser diagnostics measurements which require signal accumulation over multiple discharge pulses. Recent work using this approach includes time-resolved electron density and electron temperature measurements in ns pulse discharges in helium [5], and in O2–He mixtures in ns pulse discharges over a liquid water surface [6]. To analyze the mechanism of electron generation and decay in ns pulse discharges in helium and O2–He mixtures at the present conditions, the experimental results are compared with kinetic modeling predictions.

2. Experimental setup and data reduction

The experimental setup used in the present study is essentially the same as the one used on our previous work [5]. Briefly, the experiments have been conducted in a diffuse filament, ns pulse discharge sustained between two spherical copper electrodes 7.5 mm in diameter, separated by a 10 mm gap (see figure 1). The electrode assembly was placed into a six-arm cross glass test cell, using high-voltage vacuum feedthroughs in the top and bottom arms of the cell, with two additional arms 2 inches in diameter and 75 cm long each providing access to the focused laser beam. The discharge was generated in helium, H2–He, and O2–He mixtures at a pressure of 100 Torr. The gas mixture was flown through the cell in the axial direction at the flow rate of 2.5 slm, which corresponds to the estimated axial flow velocity of $u \approx 16$ cm s$^{-1}$. The high voltage electrode (top electrode in figure 1) was powered by a custom-built high-voltage pulse generator producing a positive polarity, double-pulse voltage waveform, with peak voltage of 3.5–4.7 kV, peak current of 13–17 A, pulse duration of ~150 ns, and time delay between the primary and the secondary pulses of several hundred ns. The pulse generator can be operated continuously at pulse repetition rates of up to 1–2 kHz. In the present work, it was operated at 90 Hz. This generated a diffuse plasma filament between the electrodes, $d \approx 2–3$ mm in diameter, well reproducible shot-to-shot. Discharge voltage and current were measured by a Tektronix P6015 high voltage probe and a Pearson 2877 current monitor.

Operating the discharge at a relatively high pressure of 100 Torr provides a compromise between sustaining a well-defined discharge filament with high electron density and filament stability. Reducing pressure would generate a more volumetric and diffuse plasma with lower electron density, which would be more difficult to characterize using the present diagnostics. On the other hand, increasing pressure would result in discharge instability development and its poor reproducibility shot-to-shot, which is critical for the present diagnostics which requires signal accumulation over multiple laser shots.

Over the last two decades, Thomson and Raman scattering have been used increasingly widely for measurements of electron density, electron temperature, and gas temperature in nonequilibrium plasmas [7–11]. In the present work, Thomson scattering measurements were conducted using a custom-built triple grating spectrometer similar to the one used in [12, 13], designed to isolate Thomson signal from Rayleigh scattering and described in detail in [5]. The scattering signal was generated by a frequency doubled Nd:YAG laser ($\lambda_0 = 532$ nm), with full width at half-maximum (FWHM) pulse duration of 10 ns and pulse energy of 500 mJ, operated at 30 Hz. The laser beam was directed axially, through fused silica windows attached to the end of the arms and set at Brewster’s angle to reduce stray light. The beam was focused on the filament centerline halfway between the electrodes, as indicated in figure 1. The scattered beam image was rotated over 90° and focused onto the entrance slit of the spectrometer. Scattering signal was collected from a ~50 micron diameter, 3 mm long volume of the discharge, which corresponds approximately to the laser beam/plasma overlap region. The data were averaged over this collection volume. In the spectrometer, a stainless steel mask blocked the Rayleigh scattering but passed the Raman and Thomson scattering spectra which are significantly wider. The spectra were taken by a PI-MAX-3 ICCD camera, using a 20 ns gate. The same camera was used to take broadband plasma emission images. Plasma background emission spectra and stray light laser scattering spectra were taken at the same conditions, with the laser and the discharge turned off, respectively, and subtracted from the raw spectra to isolate the Thomson–Raman scattering spectrum. Data points were collected starting from $t = 10$ ns after the start of the discharge current pulse, until the Thomson scattering signal became too low to detect without increasing single integration time of 20 min (i.e. when the electron number density became too low).
Electron density, electron temperature, and gas temperature (in O₂–He mixtures) were inferred from Thomson–Raman scattering spectra. Absolute calibration of experimental Thomson–Raman spectra was done by taking pure rotational Raman scattering spectra in nitrogen in the absence of the plasma, at known temperature and pressure. As discussed in our previous work [5], Thomson scattering spectra were approximated using a Gaussian fit, which assumes Maxwellian electron energy distribution function (EEDF). At the present conditions, electron density generated in the ns pulse discharge is \( n_e \sim 10^{13}–10^{14} \text{ cm}^{-3} \) (see section 4), such that ionization fraction is fairly high, \( n_e/N \sim 10^{-2}–10^{-3} \). At these conditions, the shape of EEDF is controlled primarily by electron–electron collisions, such that EEDF becomes nearly Maxwellian [14]. This was confirmed by plotting the scattering spectra in He and H₂–He versus electron energy (which is proportional to the square of the spectral shift, \( \Delta \lambda = \lambda - \lambda_0 \)) on a semilog scale, which produced near straight lines indicating the Maxwellian EEDF. In helium and H₂–He mixtures, where contribution of Raman scattering to the spectra was not a factor, electron density and electron temperature were inferred directly from the area under the best Gaussian fit to Thomson scattering spectra and its FWHM, respectively, as discussed in detail in our previous work [5]. In O₂–He mixtures, all three parameters (electron density, electron temperature, and gas temperature) were inferred simultaneously from best fit Thomson–pure rotational Raman scattering synthetic spectra. For this, O₂ rotational Raman scattering synthetic spectra (Q-branch) were calculated using accurate vibrational–rotational level energies, rotational line intensities.
3. Kinetic model

High-pressure, low-temperature oxygen–helium plasmas (primarily AC and RF driven atmospheric pressure plasma jets) have been studied rather extensively over the recent years using kinetic modeling, e.g. see [16–18]. However, modeling of ns pulse discharges in O2–He mixtures have received significantly less attention. To provide insight into kinetics of ionization and electron decay in ns pulse discharges in He and O2–He mixtures, we employed a quasi-1D kinetic model of a ns pulse discharge, using the same approach as described in our previous work [19]. The use of a 1D model, with a coordinate axis z parallel to the axis of symmetry of the discharge (see figure 1) is justified since the electrode diameter is significantly larger compared to the filament diameter, such that the electrode curvature has a relatively weak effect on the parameters in the discharge filament. Also, radial fluxes of charged species during the discharge pulse ~150 ns duration are much lower compared to the axial fluxes (in z-direction), except for a thin region in the cathode layer. At these conditions, the discharge parameters (such as the electric field and the rate of ionization) are controlled by the transport of charged species in the axial direction.

Briefly, the model incorporates time-dependent equations for number densities of electrons and ions (He+, He2+, O−, O2, O3, O+, O2+, O3+, O4+) and neutral species (He, He(3S), He2 excimers, O2(1Δg), O2(b1Σg), O2+*, O(3P), O(1D), O(1S), O3). Here O2* is a sum of three excited electronic states of O2 molecule, A3Σ∗, C1Δu, and e1Σg+. These equations are coupled to the Poisson equation for the electric field; two-term expansion Boltzmann equation for EEDF; including electron–electron collision term; electron energy equation (a moment
Boundary conditions at the electrodes are zero number densities for charged species and zero fluxes for non-excited neutral species. The secondary electron emission coefficient used is $\gamma = 0.1$. Excited species quenching probabilities at the electrodes are taken to be the same, $10^{-3}$, although the effect of surface quenching of excited species during the discharge pulse ~150 ns long and in the afterglow on a ~1 $\mu$s time scale is negligible. The electrode surface temperature is assumed to be constant, $T_s = 300$ K. Initial electron density is assumed to be very low, $10^4$ cm$^{-3}$ (varying it in the range of $10^3$–$10^6$ cm$^{-3}$ had a weak effect on breakdown moment and the predicted current waveform). The apparent diameter of the discharge filament, necessary to predict the discharge current, was determined from ICCD images of broadband plasma emission, approximately 2.3 mm. Electron impact cross sections used by the Boltzmann equation, predicting EEDF, electron mobility, and rate coefficients of electron impact processes as functions of electron temperature, are taken from Bolsig+ database [20]. Data on ion mobility versus reduced electric field are taken from [21]. Rate coefficients of electron–ion and ion–ion recombination, electron attachment and detachment, ion–molecule reactions, and neutral species reactions are taken from [22, 23].

4. Results and discussion

Figures 2 and 3 show voltage, current, and coupled energy waveforms in helium, 5% H$_2$–He mixture, and 10% O$_2$–He mixture. For all operating conditions, a double-pulse voltage waveform is generated by the pulser. The delay between the primary and the secondary voltage pulses is ~300–400 ns, depending on the gas mixture. Pulse peak voltage in helium is approximately 4.7 kV, and 3.4–3.7 kV in H$_2$ and O$_2$ containing mixtures, with peak current of 13 A in helium and 13–17 A in H$_2$–He and O$_2$–He mixtures. Energy coupled to the plasma by the primary and secondary pulses is comparable, with total coupled energy of 5 mJ/pulse in helium. In H$_2$–He and O$_2$–He mixtures, plasma generator peak voltage was adjusted to keep coupled pulse energy nearly the same, approximately 4 mJ/pulse. The experimental voltage waveforms were used as inputs in the kinetic model. Figure 3 also plots the discharge current and coupled energy waveform predicted by the model. It can be seen that predicted peak current during the primary and secondary pulses is close to the experimental data, with predicted coupled pulse energy about 20% lower compared to the measured value. However, the model consistently overpredicts the rate of discharge current rise, both after the primary pulse breakdown and during the secondary pulse (see figure 3). This discrepancy between the experimental and predicted current waveforms has also been observed in our previous work [5], where a 2D kinetic model was used. In the present work, parametric modeling calculations demonstrated that the factor that affects the predicted current pulse shape most significantly is the reduction of the ion mobility at high electric field in the cathode layer, which controls the rate of secondary electron emission from the cathode.
Figures 4 and 5 show broadband plasma emission images in helium, H₂–He, and O₂–He mixtures. All images are 100-shot averages taken with a 200 ns camera gate. Both primary and secondary pulse images are shown for each gas mixture. As can be seen, in all cases, a stable, diffuse, single filament discharge is produced, with filament diameter up to ≈3 mm (in He and H₂–He mixtures) and ≈2–3 mm (in O₂–He mixtures). Unlike in H₂–He mixtures, the filament diameter is reduced as the O₂ fraction n the mixture increases. Plasma emission also 'envelopes’ the spherical cathode and, in most cases, the cylindrical cathode stem, indicating the area occupied by the cathode spot to sustain a significant discharge current during the pulse.

Figure 6 shows a typical Thomson scattering spectrum in a 5% H₂–He mixture, taken t = 100 ns after the onset of the primary current pulse, and plotted with the best Gaussian fit used to infer the electron density, \( n_e = (1.5 \pm 0.2) \cdot 10^{14} \text{ cm}^{-3} \), and electron temperature, \( T_e = 2.02 \pm 0.2 \text{ eV} \). In H₂–He mixtures, rotational lines of the Q-branch pure rotational Raman scattering spectrum are not detected, due to the large rotational constant of H₂ resulting in a large Raman shift. In O₂–He mixtures, on the other hand, Thomson and Raman scattering spectra overlap, as illustrated in figure 7(a), showing a typical scattering spectrum in a 10% O₂–He mixture, also taken at t = 100 ns. Figure 7(a) also plots the best fit synthetic scattering spectrum, which corresponds to electron density of \( n_e = (1.7 \pm 0.1) \cdot 10^{14} \text{ cm}^{-3} \), electron temperature \( T_e = 1.6 \pm 0.1 \text{ eV} \), and gas temperature of \( T_{\text{rot}} = 300 + 40/–30 \text{ K} \). The uncertainty in electron density and electron temperature includes baseline noise in Thomson scattering spectra, statistical uncertainty, and the systematic uncertainty in N₂ and O₂ Raman cross sections. For data taken in O₂–He mixtures, the uncertainty in electron density, electron temperature, and rotational temperature inferred from the synthetic Thomson/rotational Raman scattering spectra is defined as the range within which the least squares difference between the experimental and the synthetic spectra increases by 20% compared to the minimum value. Figure 7(b) compares the experimental and the synthetic scattering spectra in the same mixture, taken in the afterglow at \( t = 5 \mu\text{s} \) after the primary discharge current rise. At this long time delay, electron density is reduced to below detection limit, due to electron–ion recombination and three-body attachment to oxygen, such that nearly the entire spectrum is due to pure rotational Raman scattering on O₂ molecules. At these conditions, as expected, the gas temperature inferred from the best fit Raman spectrum is higher, \( T_{\text{rot}} = 380 + 50/–40 \text{ K} \). The difference between the experimental and the synthetic spectra apparent in figure 7(b) is likely due to the radial temperature gradient in the heated filament in the afterglow.

As discussed in section 2, for all Thomson/Raman scattering spectra taken in the present work, the EEDF was near-Maxwellian, with a straight line fit in a semi-log plot for electron energy of up to \( \epsilon = 8 \text{ eV} \). For spectra taken in O₂–He mixtures, linear fitting was done after subtracting pure rotational Raman spectra. No systematic deviation of the EEDF from a straight line was detected for any of the data points, within the experimental uncertainty.

It is important to verify that electron density and electron temperature in the plasma are not affected by the laser pulse, due to optical breakdown, photo-ionization of excimers, or inverse Bremsstrahlung. For this, Thomson scattering measurements in a ns pulse discharge in helium at 200 Torr and considerably higher discharge pulse energy of 15 mJ, at \( t = 125 \text{ ns} \) after the discharge current rise, have been done for three different laser pulse energies, 45 mJ/pulse, 260 mJ/pulse and 585 mJ/pulse. Both electron density and electron temperature at these conditions, inferred from Thomson scattering spectra, varied within 15% measurement uncertainty. In the rest of the measurements in the present work, the laser pulse energy is approximately 500 mJ/pulse.

Figure 8 plots time-resolved electron density measured in helium and H₂–He mixtures. The inset in figure 8 shows electron density during the first 200 ns after breakdown (i.e. after
the primary pulse current onset). A rapid initial electron density rise over the first ~70–100 ns after breakdown is observed in all cases. This is followed by a partial decay, and then by a second peak, due to the double pulse voltage waveform produced by the plasma generator (see figure 2), before decaying in the afterglow. Peak electron density ranges from $n_e = 2.9 \times 10^{14} \text{ cm}^{-3}$ (1% H$_2$ in helium) to $n_e = 1.7 \times 10^{14} \text{ cm}^{-3}$ (5% H$_2$ in helium), most likely due to lower electron impact ionization coefficient in H$_2$–He mixtures, caused by additional inelastic electron impact processes, such as electronic excitation and dissociation of H$_2$ molecules. The dominant ion generated during the discharge pulse in helium is He$^+$, which is rapidly (on the time scale of several hundred ns) converted to He$^+_2$, He$^+$ + He + M $\rightarrow$ He$^+_2$ + M, such that plasma decay in the afterglow is controlled by dissociative recombination of electrons and He$^+_2$ ions. In H$_2$–He mixtures, additional ions generated during the pulse are H$^+_2$ and H$^+$, the latter converted to H$^+_3$ in the afterglow. In helium, the electron density decay in the afterglow is much slower compared to H$_2$–He mixtures, at least 2 $\mu$s before reaching detection limit of the present diagnostics, approximately $10^{13} \text{ cm}^{-3}$ (see figure 8). As the H$_2$ fraction in the mixture is increased, electron density decays more rapidly, most likely due to dissociative recombination of electrons and H$^+_2$, H$^+_3$ ions,

\begin{align}
H^+_2 + e & \rightarrow H + H, \quad (1) \\
H^+_3 + e & \rightarrow H + H + H, \quad (2)
\end{align}

which is up to an order of magnitude faster compared to dissociative recombination of He$^+_2$ ions [14],

\begin{equation}
\text{He}^+_2 + e \rightarrow \text{He}^+ + \text{He}. \quad (3)
\end{equation}

Figure 9 plots time-resolved electron temperature in H$_2$–He mixtures, at the conditions of figure 8. The inset in figure 9 shows electron temperature during the first 200 ns after breakdown (i.e. after the primary pulse current onset). In all cases, initial rise of electron temperature during breakdown is not resolved. Peak electron temperature ranges from $T_e \approx 5.5 \text{ eV}$ (in helium) to $T_e = 4.4 \text{ eV}$ (2% H$_2$ in He). Between the pulses in the two-pulse waveform, the electrons are cooled very rapidly, to $T_e \approx 0.3 \text{ eV}$, until more energy is added by the secondary discharge pulse. During the secondary pulse, a gradual electron temperature rise is detected, up to $T_e \approx 2.7–3.0 \text{ eV}$, before the electrons cool down again. Electron temperature decays to approximately the same value, $T_e \approx 0.3 \text{ eV}$, after the primary and secondary pulses, approximately 250 ns after the respective voltage peaks. This is significantly higher than the gas temperature (estimated to be $T_{\text{rot}} \sim 300–400 \text{ K}$), and suggests that electrons are heated in superelastic collisions with metastable excited helium atoms and excimers, He$^+_2$, in the early afterglow. As expected, electron temperature decays more rapidly compared to electron density, since electron–ion recombination occurs on a significantly longer time scale than electron energy loss (both elastic and inelastic), occurring in nearly every electron-neutral collision. Finally, different
timing for electron temperature rise during the secondary pulse is due to different time delays between the primary and secondary pulses for different mixtures (e.g. see figure 2).

The results in O₂–He mixtures, plotted in figures 10 and 11, exhibit trends similar to H₂–He mixtures. In O₂–He mixtures, additional ions generated during the discharge pulse are O₂⁺ and O⁺, the former converted to O₄⁺ in the afterglow. Negative ion formation during the pulse, due to dissociative attachment, O₂⁺ + e⁻ → O⁺ + O⁻, is a relatively minor effect, since the rate of electron impact ionization during breakdown greatly exceeds that of dissociative attachment. In this case, peak electron density values range from \( n_e = 3.1 \cdot 10^{14} \text{ cm}^{-3} \) (2% O₂–He mixture) to \( n_e = 1.7 \cdot 10^{14} \text{ cm}^{-3} \) (10% O₂ in He, see figure 10). Again, as the O₂ fraction in the mixture is increased, electron density between the pulses and after the secondary pulse decays more rapidly. In this case, electron density decay due to electron–ion recombination, such as

\[
O₂⁺ + e⁻ \rightarrow O⁺ + O, \tag{4}
\]

\[
O₄⁺ + e⁻ \rightarrow O₂ + O₂, \tag{5}
\]
is also accelerated by three-body electron attachment to \( \text{O}_2 \) molecules, which is known to be one of the dominant electron removal processes in high-pressure oxygen-containing plasmas and afterglow at low temperatures,

\[
\text{O}_2 + e + M \rightarrow \text{O}_2^* + M.
\]  

(6)

However, at the present conditions this effect is relatively minor since the time scale for this process, \( \tau_{\text{att}} \approx 5\text{--}100 \mu s \) for \( \text{O}_2 \) mole fraction of 1--10%, is much longer compared to that for the dissociative recombination, \( \tau_{\text{rec}} \approx 100 \text{ ns} \). Peak electron temperatures range from \( T_e = 5.5 \text{ eV} \) (helium) to \( T_e = 2.9 \text{ eV} \) (10% \( \text{O}_2 \) in helium). Similar to \( \text{H}_2\text{--He} \) mixtures, electron temperature between the pulses and after the secondary pulse decays to \( T_e \approx 0.3 \text{ eV} \), due to superelastic collisions with metastable helium atoms and excited oxygen molecules. Again, different timing for electron temperature rise during the secondary pulse is due to different time delays between the primary and secondary pulses for different mixtures.

Note that electron temperature in the afterglow appears to be about the same, \( T_e \approx 0.3\text{--}0.4 \text{ eV} \), in all \( \text{H}_2\text{--He} \) and \( \text{O}_2\text{--He} \) mixtures studied (see figures 9 and 11). This suggests that the contribution of vibrationally excited \( \text{H}_2 \) and \( \text{O}_2 \) molecules to superelastic collisions at these conditions is fairly minor compared to that of \( \text{He} \) metastables. Also, at high peak reduced electric field conditions of the present experiments (\( E/N \approx 100 \text{Td} \)), discharge energy fraction going into vibrational excitation of \( \text{H}_2 \) or \( \text{O}_2 \) diluted in \( \text{He} \) is very low.

Figures 12--14 compare electron density and electron temperature measured in helium and \( \text{O}_2\text{--He} \) mixtures with kinetic modeling calculations. It can be seen that the model predictions are generally in good agreement with the data. However, in helium the model overpredicts peak electron temperature and electron density, as well as the rate of electron density rise during the first ~100 ns after breakdown (see figure 12). As discussed in our previous work [5], this occurs since the model predictions are extremely sensitive to predicted breakdown voltage, due to a strongly non-linear dependence of ionization rate coefficient on the electric field. Underpredicting the breakdown voltage by only ~100V, i.e. underpredicting the breakdown moment by ~1--2 ns, results in significant overprediction of both electron density and rate of ionization. Due to this effect, the predicted discharge current, plotted in figure 3, peaks earlier compared to the experimental current, at higher applied voltage, which results in higher electron temperature and electron density predicted during the first ~50--100 ns of the primary discharge pulse. From the measured leak rate of the discharge cell (2--3 Torr \( \text{h}^{-1} \)) and the flow rate (2.5 slm), the estimated impurity level is approximately 10ppm. Based on kinetic modeling predictions, adding 10 ppm of air to helium at the present conditions results in a weak effect on electron swarm parameters. Specifically, the effect on electron impact ionization rate does not exceed 2%. In \( \text{O}_2\text{--He} \) mixtures, the model also somewhat overpredicts the rate of electron density decay (e.g. see figures 13 and 14).

Figure 15 compares experimental and predicted gas temperatures in the plasma during and after the discharge pulse in a 10% \( \text{O}_2\text{--He} \) mixture, inferred from pure rotational \( \text{O}_2 \) Raman scattering spectra, such as shown in figure 7. It can be seen that the temperature in the beginning of the discharge pulse is close to room temperature, within the experimental uncertainty, indicating that time delay between the discharge pulses, approximately 11 ms, is sufficient for filament cooling by diffusion and convection. At these conditions, convection and diffusion times are estimated to be \( \tau_{\text{conv}} \approx d^2/\alpha \approx 15 \text{ ms} \) and \( \tau_{\text{diff}} \approx [(d/2)(2.4)^2]/D \approx 0.4 \text{ ms} \), respectively, where \( D \approx 6 \text{ cm}^2 \text{ s}^{-1} \) is the room temperature diffusion coefficient of \( \text{O}_2 \) in helium at \( P = 100 \text{ Torr} \). Gas temperature measured 2 \( \mu \text{s} \) and 5 \( \mu \text{s} \) after the discharge pulse remains fairly low, approximately \( T = 340 \) and 380 K (see figure 15), consistent with the model prediction at \( t = 2 \mu \text{s} \), \( T = 350 \text{ K} \). Figure 16(a) plots predicted O atom number density generation by the discharge pulse at these conditions, which reaches approximately \( [\text{O}]_{\text{pulse}} = 3.2 \cdot 10^{15} \text{ cm}^{-3}/\text{pulse} \). O atom decay rate in late afterglow is controlled by radial diffusion, recombination with \( \text{O}_2 \) molecules,

\[
\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M},
\]  

(7)

with room temperature reaction rate coefficients of \( k_{\text{O}_2\text{--O}} = 6.2 \cdot 10^{-34} \text{ cm}^6 \text{ s}^{-1} \) [22], \( k_{\text{O}_2\text{--He}} = 3.4 \cdot 10^{-34} \text{ cm}^6 \text{ s}^{-1} \) [23], and reaction of O atoms with ozone,
with room temperature reaction rate coefficient of $k_{10} = 8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ [22]. The characteristic O atom decay time in these reactions is $\tau_{\text{chem}} \approx 1/(2k_9 \cdot [\text{He} \cdot [\text{O}_2]) \sim 1 \text{ ms}$, i.e. comparable to the estimated diffusion time, $\tau_{\text{diff}} \sim 0.4 \text{ ms}$. This indicates that operating the plasma generator continuously at a pulse repetition rate of ~2 kHz (with time delay between the pulses of $\tau_{\text{pulse}} = 0.5–1.0 \text{ ms}$, $\tau_{\text{pulse}} \sim \tau_{\text{diff}} \sim \tau_{\text{chem}}$) would generate quasi-steady-state O atom number density in a 10% $\text{O}_2$–He mixture of ~$10^{15} \text{ cm}^{-3}$. Finally, figure 16(b) plots predicted number densities of $\text{He}^+$ atoms, $\text{O}$ atoms, and $\text{O}_2(a^1\Delta)$ molecules during and after the discharge pulse in a 1% $\text{O}_2$–He mixture. It can be seen that at this low $\text{O}_2$ mole fraction, $\text{He}^+$ is by far the dominant excited species, exceeding $\text{O}$ atoms and $\text{O}_2(a^1\Delta)$ by about two orders of magnitude.

5. Summary

Time evolution of electron density and electron temperature in a nanosecond pulse, diffuse filament electric discharge in $\text{H}_2$–He and $\text{O}_2$–He mixtures at a pressure of 100 Torr is studied by Thomson/rotational Raman scattering and kinetic modeling. The discharge is sustained between two spherical electrodes separated by 1 cm and powered by a high voltage pulse generator generating ~150 ns duration pulses with peak voltage of 3.5–4.7 kV, operating at a pulse repetition rate of 90 Hz. At these conditions, pulse energy coupled to the plasma filament 2–3 mm in diameter is 4–5 mJ/pulse, resulting in specific energy loading of up to ~0.3 eV/molecule. In all gas mixtures tested, a rapid initial rise of electron temperature and electron density during the discharge pulse (over ~100 ns), followed by the decay in the afterglow (over ~100 ns–1 µs), are observed. The electron density in the afterglow decays more rapidly as $\text{H}_2$ or $\text{O}_2$ fraction in the mixture is increased. In $\text{He}/\text{H}_2$ mixtures, this is likely due to more rapid recombination of electrons in collisions with $\text{H}_2^+$ and $\text{H}_3^+$ ions, compared to recombination of electrons with $\text{He}_2^+$ ions. In $\text{O}_2$/He mixtures, the rate of rapid electron density decay is affected by recombination with $\text{O}_2^+$ and $\text{O}_3^+$ ions as well as by three-body attachment to oxygen molecules, although at the present conditions the effect of attachment is relatively minor. At the present conditions, peak electron number densities are in the range of $n_e = (1.7–3.1) \times 10^{14} \text{ cm}^{-3}$, depending on gas mixture composition. Peak electron temperatures are in the $T_e \approx 2.9–5.5 \text{ eV}$ range. Electron temperature in the afterglow decays to approximately $T_e \approx 0.3 \text{ eV}$, considerably higher compared to gas temperature of $T = 300–380 \text{ K}$, inferred from rotational structure of $\text{O}_2$ Raman scattering spectra of $\text{O}_2$, due to superelastic collisions.

The experimental results in helium and $\text{O}_2$–He mixtures are compared with 1D self-consistent kinetic model predictions, showing good agreement. The results provide insight into kinetics of ionization, recombination, and electron attachment in $\text{H}_2$–He and $\text{O}_2$–He plasmas, as well as data for kinetic model validation. The modeling predictions suggest that a ns pulse discharge operating at a pulse repetition rate of ~1–2 kHz can generate quasi-steady-state O atom number densities of up to $10^{15} \text{ cm}^{-3}$, at fairly low gas temperatures. The present work provides experimental data for validation of higher dimensionality kinetic models of transient molecular plasmas at high specific energy loadings.

Acknowledgments

This research has been supported by US DOE Center for Predictive Control of Plasma Kinetics: Multi-phase and Bounded Systems and by US DOE Center for Exascale Simulation of Plasma-Coupled Combustion (XPACC).

References

[1] Heaven M C 2010 Recent advances in the development of discharge-pumped oxygen-iodine lasers Laser Photonics Rev. 4 671–83