A global model of cylindrical and coaxial surface-wave discharges

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Abstract

A volume-averaged global model is developed to investigate surface-wave discharges inside either cylindrical or coaxial structures. The neutral and ion wall flux is self-consistently estimated based on a simplified analytical description both for electropositive and electronegative plasmas. The simulation results are compared with experimental data from various discharge setups of either argon or oxygen, measured or obtained from the literature over a wide range of pressure and power, for a continuous and a pulse-modulated power input. A good agreement is observed between the simulations and the measurements. The contribution of the wall flux on the net loss rates is quantified for a variety of species in different discharge setups. A coaxial plasma line is further investigated to reveal the detailed behaviour of plasma properties with respect to input power and pressure.

Keywords: surface-wave discharge model, global model, computational plasma physics

(Some figures may appear in colour only in the online journal)
One-dimensional models are used for the axial [8–10] as well as radial characteristics [11] and complemented with a series of zero-dimensional kinetic models [12, 13] to provide a wider insight into various aspects. A variety of more detailed models are developed for a feeding gas of argon [14–16], hydrogen [17] and oxygen [18] that are often associated with numerically expensive simulations. The focus of these studies is mostly on the cylindrical structures and the analysis of the coaxial structures with similar models are relatively rare. A computationally efficient zero-dimensional alternative to these models is a transient volume-averaged global model [18–25] that additionally averages over the position variable of the phase space. The model describes the volume-averaged plasma quantities via reaction rates in the plasma volume as well as effective particle flux rates at the chamber walls. It additionally provides a temporal resolution of these quantities which is advantageous for the pulse-modulated power inputs. However, the volume-averaged global models are rarely implemented for the considered surface-wave discharges. An agreement is obtained with the measurements in surfatron oxygen plasma as well as with spatially resolved models in a microwave reactor by a recent implementation [18]. An important quantity in these types of models is the wall flux rate. The implementation in [18] still requires a self-consistent estimation of the ion wall flux for both the cylindrical and coaxial surface-wave discharges which is addressed in the content of the current study.

The volume-averaged global models are mostly implemented in comparatively very low pressures [26], probing a variety of aspects [22, 25], where the ion wall flux rates are analytically calculated based on Bohm point edge-to-centre ratios. An edge-to-centre ratio at the lower edge of the low-pressure regime is analytically calculated for argon [27] and later joined with a high-pressure diffusion solution to cover a larger pressure range [19]. The derivations are heuristically generalized for the electronegative plasmas in the asymptotic limits of the degree of electronegativity [28–30] and added with an ansatz [20]. The ansatz is later modified for a better accuracy [31] and one region parabolic profile is often neglected [22, 24, 25, 32], since the flattening of the core becomes more important with the pressure [20]. Axial edge-to-centre ratios are recently benchmarked against spatially-resolved models in argon [33], and proposed in a new form for electropositive [34] and electronegative discharges [35]. Beside the ion losses, neutral wall flux for reflective wall might play a very important role on the plasma [19, 22]. The neutral wall flux is either estimated for various geometries [36] or calculated by a simpler derivation [20, 24, 37].

The aforementioned edge-to-center ratios can be partially adaptable in the considered pressure regime of the cylindrical structures, for example, for the argon ion wall flux rate. However, they are not directly applicable to the surface-wave discharges, since the underlying assumptions of the earlier derivations are no longer valid in (1) the structure of the electronegativity, (2) the detachment dominated negative ion loss mechanism of oxygen, (3) the unique axial characteristics of the surface-wave discharges and (4) the coaxial geometry. The derivations of the edge-to-center ratios assume electronegativity profiles that are valid at low pressure and the profiles in the considered pressure regime differ [38, 39]. These derivations neglect the role of the negative ion detachment with the assumption of recombination dominated negative ion loss rate, however, the detachment is the dominant loss mechanism in oxygen within the pressure range of interest [40]. They do not consider the axial ion profiles of the surface-wave discharges and the radial structure of the coaxial plasmaline. An analytical derivation of the edge-to-center ratios is required for a proper global model of the surface-wave discharges.

In this study, we consider the stationary and pulse-modulated surface-wave discharges of cylindrical and coaxial structures for a feeding gas of either argon or oxygen. We analytically estimate ion and neutral edge-to-centre ratios in the considered pressure regime for an accurate volume-averaged global model analysis. The computational results are compared with a variety of measurements and a good agreement is obtained. The behaviour of the coaxial plasmaline is presented for a range of input power 0.3–1.5 kW and pressure 15–80 Pa. The considered setups are given in section 2 including all the necessary input data for the model. The analytical derivations of the wall flux rates for both ions and neutrals as well as the particle and energy balance equations of the global model are explained in section 3. The results are given in section 4 whereas conclusions and discussion are presented in section 5.

2. Setup

A series of surface-wave discharges of either a cylindrical or a coaxial structure are considered. The plasma dimensions, operation parameters as well as the feeding gas of each setup that are used as input in the model are given in table 1. A Roman number is assigned to each setup that is used for reference throughout this study. The outer radius of the both structures is denoted by $R$ and interior radius in the case of the coaxial structure is denoted by $R_p$. The axial plasma dimension is represented by $L$ and the plasma volume is represented by $V$. The feeding gas is either argon or oxygen and each setup differs in dimension as well as the operation parameters.

The operation parameters cover a pressure range of 15–2000 Pa and an input power range of 45–2000 W with either continuous or pulse-modulated power input. The discharges are in the collisional regime $\lambda_e < (L, 2R)$ [39], where $\lambda_e$ is the ion mean free path, or in an alternative stricter form $\lambda_e < \sim (L/2, R)(T_e/T_R)$, which is assigned to the high-pressure regime of the conventional global model implementation [45]. The discharges are axially large, $L \gg R$, and we frequently use this fact in the simplifying assumptions of the physical model.

The value of the power transfer efficiency is important to accurately define the absorbed power and it significantly alters the plasma behaviour. The cylindrical and coaxial structures have different power transfer efficiencies. In the former structure, the power input is completely absorbed by the plasma and the power transfer efficiency is $\beta = 1$. The value is estimated from simulation results [16, 18] by calculating the net power leaving the plasma boundaries and comparing it to the
The operation of the power input is either continuous (con.) or pulse-modulated (pul.). The parameters and measurements are mostly obtained from the corresponding reference under each column. An exception is the experimental data of setup V, that are recently measured for the current study.

| (I) Type | (II) Gas | (III) Gas | (IV) Type | (V) Type |
|---------|----------|----------|----------|----------|
| Cylindrical | Ar | O₂ | Ar | Ar or O₂ |
| R (m) | 3.0 × 10⁻³ | 8.0 × 10⁻³ | 8.0 × 10⁻² | 35.0 × 10⁻³ | 43.0 × 10⁻³ |
| L (m) | 33 × 10⁻² | 20, 34 × 10⁻²(a) | 49.0 × 10⁻² | 40.0 × 10⁻² | 30.7 × 10⁻² |
| P (Pa) | 2000 | 62,7,133.3 | 50 | 800 | 15–80 |
| Q (sccm) | 45 | 40–107 | 2000 | 400 | 300–1500 |
| T₀ (K) | 800 | 300 | 375 | 0 | 100–200 |
| β | 1.00(b) | 1.00(b) | 1.00(b) | 0.45 | 0.30–0.15(e) |
| P opr. | con. | con. | pul. | con. | con. or pul. |
| meas. | RyS, TS | ML, A | TALIF | TS | LP or OES |
| Ref. | [41] | [42] | [43] | [15, 44] | [1] |

(a) We assume that the plasma length does not drastically change for the considered pressures.
(b) Obtained from [18].
(c) Obtained from simulation results in [15].
(d) The gas temperature linearly increases with input power.
(e) It is estimated with a lower value than the calculation by [15] due to the structural differences. The calculation shows that the power transfer efficiency β decays with input power.

3. The physical model

In order to describe the surface-wave discharges, a volume-averaged global model [26] is used within the multi-fluid plasma treatment [46]. In the model, we adapt two-temperature formalism that assigns different temperatures to the plasma electrons and heavy particles. The model assumes an approximate spatial homogeneity inside the plasma volume and converts the spatially-resolved description into a zero-dimensional representation with a significant reduction of the numerical load. The chemical kinetics defines the local interactions between the plasma species while the wall flux rates determine the transport and the plasma-wall interactions. Conventionally, the wall flux rates are heuristically estimated at the Bohm point from the asymptotic analytical solutions of simplified one-dimensional description at comparatively much lower pressures [20, 30]. Following a similar approach, a set of necessary wall flux rates are analytically estimated for the positive ions and the neutral particles in the considered pressure regime. The negative ion wall flux is assumed to vanish due to the sheath potential drop. In the following, the wall flux rates are initially derived based on a one-dimensional simplified description and later the global model is described. It is instructive to compare derivations to their analogues used in the low-pressure radio-frequency plasma. For the sake of such a comparison, an edge-to-centre formalism is adapted, in contrast to an earlier study [18].
3.1. Derivation of the wall flux rates

The validity of the collisionless models [20, 27] is violated in the considered collisionality regime and a constant diffusion model is adopted instead [38, 45]. The one-dimensional model is based on the drift-diffusion formulation, where the drift is due to the ambipolar electric field, and the ambipolar diffusion simply reduces to the regular diffusion for the neutrals. The axial gradient and the axial wall flux are neglected due to the large length to radius ratio of the surface-wave discharges $L \gg R$. Then, on a reference frame with a vanishing net mass flow velocity, steady-state particle continuity equation takes the form

$$
\frac{1}{r} \frac{d}{dr} \left( r D_i \frac{dn_i}{dr} \right) + S_i = 0,
$$

where $r$ is the radial position, $i$ denotes either a neutral with a reflective wall or a positive ion, $n_i$ is particle density, $D_i$ is the diffusion coefficient and $S_i$ is the source.

3.1.1. Wall flux estimation for positive ions. The ambipolar diffusion is defined by the multiple-ion Fick like diffusion coefficient [47], estimated by using a self-consistent diffusion formulation. The expression can be equivalently derived in the drift-diffusion formulation by employing the assumption of Boltzmann equilibrium electrons [48]. Together with the assumption $\nabla n_i/n_i^+ \approx \nabla n_e/n_e$ ($n_i$ and $n_i^+$ are the electron and positive ion densities, respectively) [18, 39] the ambipolar diffusion of the positive ion $i$ takes the form

$$
D_{i+} = D_i (1 + T_e/T_i),
$$

where $T_e$ is the electron temperature and $T_i$ is the ion temperature. Then assuming an approximate thermal homogeneity and using the quasineutrality constraint, the particle continuity equation of a positive ion $i$ is

$$
\frac{d^2 n_i^+}{dr^2} + \frac{1}{r} \frac{dn_i^+}{dr} + \frac{\nu_i^+}{D_{i+} (1 + \alpha)} n_i^+ = 0,
$$

where $\nu_i^+$ is the ionisation frequency and $\alpha$ is the degree of electronegativity. Here the ion recombination is neglected and $\alpha = 0$ denotes the electropositive plasma.

In this form, an estimation is required for the spatial profile of the degree of electronegativity that can be generally characterized by the collisionality. The analyses at lower collisionality—$\lambda_i > (L/2, R)(T_i/T_e)$—show that the value of the central degree of electronegativity $\alpha_0$ defines the spatial structure of the discharge. At low values of $\alpha_0$, the plasma is structured with a parabolic electronegative core surrounded by an electropositive edge [28]. The parabolic core enlarges and flattens in the discharge center with increasing electronegativity [29, 30, 49]. Such a behaviour of the degree of electronegativity at asymptotic values of $\alpha_0$ constitutes the underlying assumptions in the derivation of the edge-to-center ratios [20]. However, this behaviour substantially changes in the considered collisional regime—$\lambda_i < (L/2, R)(T_i/T_e)$. A ratio of the attachment to the ionization frequency $P = \frac{\nu_i^+}{\nu_i^{+\alpha}}$ defines the spatial dependence of the degree of electronegativity ($\mu_i$ and $\mu_L$ are the mobilities of positive and negative ions, respectively) [38, 39]. In the asymptotic limits of very small and very large values of $P$, $\alpha$ is spatially homogeneous and otherwise piecewise homogeneity is a valid assumption as a good approximation [38, 39, 50, 51]. Consequently, we assume that $\alpha$ is spatially homogeneous, where the piecewise homogeneity does not alter the general solution.

For a homogeneous degree of electronegativity, the general solution of equation (3) can be written as

$$
n_i^+(r) = C_1 \mathcal{J}_0(\chi r/R) + C_2 \mathcal{Y}_0(\chi r/R),
$$

where $J_0, Y_0$ are the zeroth order Bessel functions of the first and the second kind, $\chi C_1, C_2$ are the constants to be fixed by the boundary conditions as well as the normalization. The solution is subjected to the boundary conditions $n_i^+(r = 0) = \infty$, $n_i^+(r = R) = 0$ for cylindrical and $n_i^+(r = R) = n_i^+(r = R_p) = 0$ for coaxial plasma. The particular solution in cylindrical structure is in agreement with the analytic estimations in the asymptotic limits of very large [50] and very small values of $P$ [38, 51]. As a caveat, the parameter regimes favoring electron-ion or ion-ion recombination introduce nonlinear terms in equation (3) and disturb the solution. The ion loss reactions such as the formation of argon excimer ion, (reaction 31 of table B1) do add an extra term to equation (3), but they do not alter the general solution.

In the cylindrical structure, the ion flux density at the Bohm point can be written in the form

$$
\Gamma_i^{\text{h}} = u_{iB} h_{iB} n_{iB},
$$

where $r_{hB}$ is the radial Bohm point, $n_{iB}$ is the central ion density, $h_{iB}$ is the edge-to-centre ratio of the cylindrical structure and $u_{iB}$ is the electropositive Bohm velocity. An estimation of the edge-to-centre ratio is

$$
h_{iB} \approx \frac{1}{1 + \alpha_0} \left( \frac{u_{iBE}/u_{iB}}{\chi_0 / \chi_0 D_i + J(\chi_0)} \right)^{1/2},
$$

where $\chi_0$ is the first root of $J_0$, $u_{iBE}$ is the Bohm velocity modified by the electronegativity—see section 3.1.2—and $1/(1 + \alpha)$ is the normalization in the electronegative discharges [19]. Equations (6) and (5) are valid in the electropositive plasma for a vanishing degree of electronegativity.

An analogue of the edge-to-centre ratio that is used in the low-pressure plasma models ($\lambda_i > (L/2, R)(T_i/T_e)$) is given by the ansatz $h_{iB} = ((h_{iB,0})^2 + (h_{iB,0})^2)^{1/2}$ [25, 32] together with

$$
h_{iB,0} \approx 0.8 \frac{R}{\lambda_0} \left( 4 \frac{R}{\lambda_i} + \left( \frac{0.8 R_{iB}}{\chi_0 / \chi_0 D_i + J(\chi_0)} \right)^{1/2} \right)^{1/2},
$$

$$
h_{iB,\alpha} \approx \frac{T_i}{T_h} \left( \frac{T_e}{T_h} \right)^{1/2} \left( \frac{15}{56} \frac{v_{ti}^+}{n_{ti} n_{ti}^{-3/2}} \right)^{-1},
$$

where a bar notation is used to discriminate from equation (6). Here, $n_-$ is the negative ion density, $v_{ti}^+$ is the mean thermal...
velocity, \( k_{\text{ion-ion}} \) is the rate coefficient of ion-ion recombination and \( \lambda_i \) is the ion mean free path. The first term of the ansatz \( h_{IR,a}^+ \) denotes a parabolic electronegative core surrounded by an electropositive edge and it is valid at a low degree of electronegativity for a large range of collisionality regimes [45]. The second term \( h_{IR,e}^+ \) denotes a single electronegative region of a heuristic flat-topped description and it is valid at a large degree of electronegativity for recombination dominated negative ion loss [40].

The edge-to-centre ratio \( h_{IR,a}^+ \) is equivalent to \( h_{IR}^+ \) in the considered collisional regime. The ratio \( h_{IR,a}^+ \) is also alternatively applicable in this regime since it covers a large range of collisionality and the lower asymptotic limits of both \( P \) and \( \alpha_0 \) are substitutes for each other [38]. A non-structured highly electronegative plasma that is heuristically expressed by \( h_{IR,e}^+ \) [29] is already contained in \( h_{IR}^+ \) with the assumption of spatially invariant degree of electronegativity at a large value of \( P \) in the collisional regime [39]. Additionally, a non-structured region does not necessarily require a large degree of electronegativity in a collisional plasma [38, 39] as imposed by \( h_{IR,e}^+ \) and considered discharges are not strongly electronegative with a maximum value of \( \alpha = 12 \). As a result, the ratio \( h_{IR,e}^+ \) is not strictly adapted in a similar ansatz in the collisional regime. A numerical comparison of \( h_{IR}^+ \) and \( h_{IR,e}^+ \) is given in section 4 for the considered cylindrical plasma sources.

The coaxial structure has multiple Bohm points assigned to each radial boundary and the positive ion flux densities at these Bohm points can be written as

\[
\Gamma_1^{+} = u_B h_{IR}^{+} \text{n}_i, \\
\Gamma_2^{+} = -u_B h_{IR}^{+} \text{n}_i
\]

(8)

where \( u_B \) denotes the Bohm point near the outer boundary at \( R, \) \( r_B \) is the Bohm point near the inner boundary at \( R_p \) and the negative sign at \( r_B \) is due to the direction of the radial unit vector. Similar to the cylindrical structure, the radial edge-to-centre ratio of each radial boundary is derived as

\[
h_{IR}^+ \approx \frac{1}{1 + \alpha} \left( \frac{u_{\text{BE}}}{u_B} \right) \left( 1 + \frac{R u_{\text{BE}}}{\gamma D_1 \chi (\chi C_1 + C_2 Y_{\text{BE}})} \right)^{1/2},
\]

\[
h_{IR}^+ \approx \frac{1}{1 + \alpha} \left( \frac{u_{\text{BE}}}{u_B} \right) \left( 1 + \frac{R u_{\text{BE}}}{\gamma D_1 \chi (\chi C_1 + C_2 Y_{\text{BE}})} \right)^{1/2},
\]

(9)

where \( \chi, C_1 \) and \( C_2 \) are defined by the normalization and the boundary conditions.

3.1.2. Bohm velocity in an electronegative plasma. A new expression is required for the Bohm velocity in the presence of the negative ions. In order to calculate this expression, it is commonly assumed that the negative ions, denoted by \( \text{n}_i \), are in Boltzmann equilibrium [52] at low-pressure

\[
T_i \n_i / n_i = T_i n_i / n_e.
\]

(10)

This assumption introduces an additional factor to the Bohm velocity [45, 53]

\[
\left( \frac{1 + \alpha}{1 + \alpha^2} \right)^{1/2},
\]

(11)

where \( \gamma \) is the ratio of electron to the negative ion temperatures and \( \alpha_2 \) is the degree of electronegativity at the sheath.

The validity of the Boltzmann equilibrium fails at high-pressure [30, 54] and an alternative assumption can be utilised instead [39, 55]

\[
\n_i / n_i = \n_j / n_e.
\]

(12)

This assumption completely eliminates the additional factor on the Bohm velocity by simply equating \( \gamma \) to unity. The transition between these two assumptions can be defined by the condition of attachment dominance [48]

\[
\tau_{\text{an}} K_a > 1
\]

(13)

where \( \tau_{\text{an}} \) is the time-scale of the ambipolar diffusion and \( K_a \) is the electron attachment frequency. The following form for the Bohm velocity is used based on this condition

\[
u_{\text{BE}}/u_B = \left\{ \begin{array}{ll}
\left( \frac{1 + \alpha}{1 + \alpha^2} \right)^{1/2} & \text{if } \tau_{\text{an}} K_a \leq 1, \\
1 & \text{if } \tau_{\text{an}} K_a > 1,
\end{array} \right.
\]

(14)

where the assumption of the spatially homogeneous degree of electronegativity is implemented. A comparison of these expressions on the computational results is discussed in section 4.

3.1.3. Wall flux estimation for neutrals. The axial gradients and the axial wall flux are neglected due to the large length to radius ratio. Assuming that the neutral source \( S_i \) is radially homogeneous as an approximation [20, 37], the stationary neutral continuity equation can be written as

\[
\frac{1}{r} \frac{dr}{dr} \left( r \frac{d n_i^N}{dr} \right) + \frac{S_i}{D_i} = 0,
\]

(15)

where \( n_i^N \) is the neutral density with a reactive wall, \( S_i \) is the source and \( D_i \) is the diffusion and superscript \( N \) represents the neutral particles. The general solution can be written as

\[
n_i^N(r) = C \left( 1 - \frac{r^2}{a^2} + b \ln(r) \right).
\]

(16)

where \( C, a \) and \( b \) are the constants defined by the normalization and the boundary conditions. The flux boundary conditions are set on the chamber walls based on the reactivity of the wall material and a finite solution is imposed at the radial centre of the cylindrical structure.
The flux boundary condition at the radial wall of a cylindrical structure is [36]
\[
\left. \left( -D_r \frac{dn_i^N}{dr} \right) \right|_{r=R} = \left. D_r n_i^N \right|_{r=R} \frac{1}{l_{IR}}, \tag{17}
\]
where \(l_{IR}\) is the linear extrapolation length assigned to the wall. The linear extrapolation length can be written as [36]
\[
l_{IR} = \frac{2D_r}{v_i} \left( 2 - \frac{\gamma_{IR}}{\gamma_{IR}} \right), \tag{18}
\]
where \(\gamma_{IR}\) is the wall reaction probability and \(v_i\) is the thermal velocity. The boundary conditions of a cylindrical structure set \(b=0\) and \(a^2 = R^2 + 2RL_{IR}\) and reduce the neutral wall flux density to the form
\[
\Gamma_i^N \bigg|_{IR} = \frac{D_r n_i^N}{l_{IR}} n_{i0}, \tag{19}
\]
where \(n_{i0}\) is the density at the radial centre and neutral edge-to-centre ratio is
\[
h_{IR}^N = \left( 1 + \frac{R}{2l_{IR}} \right)^{-1}, \tag{20}
\]
An expression is similarly derived by Kim et al [20] for radially large cylindrical plasma chambers, \(R \gg L\). Although, the neutral continuity equation is governed axially for such a chamber, the derived edge-to-centre ratio is equal to \(h_{IR}^N\) when the discharge radius \(R\) and the length \(L\) are interchanged. A net wall flux rate is also estimated by Chantry [36] ignoring the source term of the continuity equation. This rate can be written in the form of equation (19) with the following edge-to-centre ratio
\[
h_{IR}^N = \left( 1 + \frac{\Lambda_0}{l_{IR}} \right)^{-1}, \tag{21}
\]
where \(\Lambda_0\) is the effective diffusion length and a bar notation is used to distinguish from equation (20). For an axially large cylindrical discharge, \(L \gg R\); this ratio can be approximated by \(h_{IR}^N \approx \left( 1 + \frac{R}{2\Lambda_0} \left( \frac{2}{2.405} \right)^2 \right)^{-1}\) that differs from \(h_{IR}^N\) only with a factor of \((2/2.405)^2\) in the second term. A further numerical comparison of the considered plasma sources is provided in section 4.

The flux boundary conditions of the coaxial structure on the radial walls \(R\) and \(R_p\) can be similarly written in the form
\[
\begin{align*}
\left. \left( -D_r \frac{dn_i^N}{dr} \right) \right|_{r=R} &= \left. D_r n_i^N \right|_{r=R} \frac{1}{l_{IR}}, \\
\left. \left( -D_r \frac{dn_i^N}{dr} \right) \right|_{r=R_p} &= -\left. D_r n_i^N \right|_{r=R_p} \frac{1}{l_{IR}^p},
\end{align*} \tag{22}
\]
where the linear extrapolation length generally differs between the inner and outer walls due to distinct reaction probabilities of the wall materials. These boundary conditions set non-zero values for the constants \(b\) and \(a\) that depends on the positions and the extrapolation lengths of the walls. Then the wall flux densities of the coaxial structure are
\[
\begin{align*}
\Gamma_i^N \bigg|_{R} &= \frac{D_r n_i^N}{l_{IR}} n_{i0}, \\
\Gamma_i^N \bigg|_{R_p} &= -\frac{D_r n_i^N}{l_{IR}^p} n_{i0}.
\end{align*} \tag{23}
\]

Analytically obtaining the values of \(b\) and \(a\) from the flux boundary conditions (equation (22)) and using the general solution (equation (16)), the inner and outer edge-to-centre ratios with a normalization constant \(C\) are
\[
\begin{align*}
h_{a}^N &= C \frac{l_{IR} R_p^2 R_p (R_p - R)(R_p - R) R^2 \ln \left( \frac{R}{R_p} \right)}{l_{IR}^p R_i^2 (R_i - R) (R_i - R) R_i^2 \ln \left( \frac{R}{R_i} \right) + l_{IR} R^3 + 2l_{IR} R^2}, \\
h_{b}^N &= C \frac{l_{IR} R_i^2 R_i (R_i - R) R_i^2 \ln \left( \frac{R}{R_i} \right) + l_{IR} R_i^3 + 2l_{IR} R^2}{l_{IR} R_p^2 R_p (R_p - R) (R_p - R) R_p^2 \ln \left( \frac{R}{R_p} \right) + l_{IR} R_i^3 + 2l_{IR} R^2}. \tag{24}
\end{align*}
\]

The ratio at each wall depends on the positions and the reactive properties of the both walls as well as the transport properties of the species \(i\).

### 3.2. The global model

The plasma is described by the volume-averaged particle and electron energy continuity equations with an assumption of Maxwellian electron energy distribution function. The plasma sheath is ignored in the model and it is considered only in estimating energy loss due to ion wall flux [45]. The simulations are sensitive to the gas temperature and their accurate estimation is essential in the model. The gas temperature is obtained from already available data of each setup and provided as an input to the model. In the paper, the following unit convention is adopted for the temperatures; the electron temperature is given in eV and the gas temperature is given in K, unless stated otherwise. All the input data required by the model is given in table 1 for each simulated discharge. It should be noted that lack of necessary input data would restrict a self-consistent analysis of the plasma source within a parameter range of desire. Here, the microwave excitation frequency is not a direct input parameter of the model, since the absorbed power is the conventionally relevant quantity. A detailed investigation on the role of the excitation frequency via global models should include its influence on the power transfer efficiency that is out of the scope of the current study.

#### 3.2.1. Volume-averaged particle continuity equation

The volume-averaged particle continuity equation is written in the form
\[
\frac{dN_i}{dr} = \sum_j W_{ij} R_j \bigg|_r - \sum_j W_{ji} R_j \bigg|_{r}, \tag{25}
\]
where \(i\) denotes the particular species, \(N_i\) is the volume-averaged particle density, \(j\) denotes a particular source channel with a rate \(R_j\) and a net stoichiometric coefficient \(W_{ij}\). The
The wall energy loss is [45]

\[ Q_w = \sum_{j \in \text{ions}} (E_P + \varepsilon_e + \varepsilon_i) R_{w}^j. \]  

(29)

where \( E_P \) is the plasma potential, \( \varepsilon_e \) is the mean energy loss per electron and \( \varepsilon_i \) is the sheath potential. The plasma potential is [45]

\[ \varepsilon_i = \frac{1}{2} \left( \frac{u_{\text{BE}}}{v_e} \right)^2 T_e, \]  

(30)

where \( u_{\text{BE}} \) is the Bohm velocity of the dominant ion while the mean energy loss per electron is \( \varepsilon_e = 2T_e \). We use an estimation of the sheath potential by Thorsteinsson et al [57] together with the assumption of the spatially homogeneous degree of electronegativity

\[ \varepsilon_i \approx \ln \left( 1 + \alpha \left( \frac{v_e}{v_0} \right) \right) \]  

(31)

where \( v_e \) and \( v_0 \) are the mean thermal velocities of electrons and ions, respectively. The assumption of the Boltzmann equilibrium of the negative ions—or its high-pressure alternative \( \n_i n_j = \n_j n_i \)—does not significantly affect the sheath potential estimation except at very large degree of electronegativity [57]. The sheath and plasma potential expressions for the electropositive gas are obtained for a vanishing degree of electronegativity.

4. Results

A variety of cylindrical and coaxial surface-wave discharges operated over a wide range of power and pressure are simulated and the simulation results are compared with the available spatially-averaged measurements in section 4.1. An important feature of the considered discharges is stronger spatial gradients compared to low-pressure discharges (conventional implementation regime of the global models). Therefore, the spatially-averaged measurements are mostly provided in their original form for a detailed view of the profile. The operation parameters of the simulated discharge setups are given in table 1. The measurements are denoted by symbols, where filled symbols are reserved for their spatial-average, and the calculations are shown by lines or line-points. A discussion on the state of certain model parameters and on the analytically estimated radial profiles as well as a comparison of the edge-to-centre ratios against their low collisionality analogues are also provided. A further investigation of the coaxial plasma of interest, shown in column V of table 1, is given in section 4.2 by providing the variation of plasma quantities within a range of input power and pressure.

4.1. Benchmarking against measurements

The measurements and the calculations of the cylindrical structure are shown in figure 1 for a series of distinct discharges fed with either argon or oxygen. The operation parameters of each setup are provided in table 1—under columns I, II, and III. Figure 1(a) shows the axially-resolved and axially-averaged
electron and argon densities as well as the electron temperature in a stationary argon surfatron (I) [41]. Figure 1(b) shows axially-averaged $e$, $O_2(a_2^1\Delta_g)$ and $O_2$ densities of a stationary oxygen surfatron (II) [42] for a set of power input and pressure values. Figure 1(c) shows transient O density on a pulse-modulated microwave source of SLAN type of oxygen (III) [43]. We observe a good agreement between the spatially-averaged measurements and the simulation results, except for the electron density of the argon surfatron in figure 1(a). The argon surfatron shows radial contraction at the end of the plasma column [44] and this might cause such a deviation. Furthermore, the measurements are performed at the radial center, corresponding to the local density maximum, and it might induce a large spatial-average neglecting the role of the radial variation. The simulation results of the oxygen surfatron show a better agreement compared to the earlier results of a rough ion edge-to-centre ratio estimation [18]. However, a transient profile identical to the earlier result [18] appear in the microwave source of SLAN type. The profile deviates from the measurements by the steep rise of the O density and the initial part of the decay rate, the former being also computationally observed in a milder form by Georg et al. [43]. Since the discharge has a relatively large radius and connects to a cubic chamber, such a deviation might be due to temporal variations in the appointed plasma volume and a strong localization of the ionization [58].

The simulation results and the measurements of the coaxial structures IV and V —see table 1— for a feeding gas of argon are shown in figure 2. The radially-resolved and radially-averaged electron density and temperature are shown in figure 2(a) for a stationary plasmiline IV [15]. The same type of data is shown in figure 2(b) in the plasmiline of interest V at 30 Pa for an input power of 300 W with the gas temperature of 500 K and the gas flow rate of 100 sccm, whereas axially-resolved and axially-averaged versions are shown in figure 2(c). We observe that the radial variation is much more amplified than the axial variation and the axially-resolved measurements have very similar value with their axial-averages. In this respect, they differ from setup I with the axial gradients and a steep decay only exists in a much smaller gap. The simulation results show a good agreement with the stationary radially- and axially-averaged measurements.

The measurements on the discharge setup V of either argon or oxygen for continuous and pulse-modulated powers are shown in figure 3 together with the simulation results. The radially-resolved and radially-averaged electron density and temperature in continuous power oxygen plasma are given in figure 3(a). The power input is 600 W at a pressure of 25 Pa and the gas temperature is 500 K with a gas flow rate of 200 sccm. The transient electron density and temperature of the pulse-modulated discharge in argon and oxygen are shown in figures 3(b) and (c), respectively. The pressure is 30 Pa for argon and 25 Pa for oxygen discharge both at a gas temperature of 900 K and the peak power input for both pulse-modulated measurements is 1500 W. The gas flow rates are 100 sccm in argon and 200 sccm in oxygen. The simulation results agree well with the radially-averaged stationary as well as transient measurements. However, the electron decay in the argon afterglow suggests considerably smaller decay rate compared to the experimental observation. The estimation of the afterglow edge-to-centre ratio to the unity—for example, after the electrons thermally equilibrate with the background gas—imposes much faster decay rate. However, such an assumption is not preferred due to the lack of data in the afterglow spatial structures, regarding validity requirements as well as the resultant sudden change in the decay rate.

![Figure 1](image_url)

Figure 1. The measurements performed on distinct surface-wave discharges of cylindrical structures I [41], II [42] and III [43] of table 1 and the simulation results (line or line-points). The simulation results are volume-averaged and they are comparable to the spatially-averaged measurements. (a) Axially-resolved $e$ (△) and Ar (○) densities as well as the electron temperature $T_e$ (square symbol) in an argon surfatron (I) together with their axial averages—denoted by △, ● and □ respectively. (b) Axial-averages of $e$ (▲), $O_2$ (●) and $O_2(a_2^1\Delta_g)$ (■) density measurements in an oxygen surfatron (II). (c) Transient O density measurements in a microwave source of SLAN type with a pulse-modulated power input (III).
We also observe that the electron temperature decays much slower as its value falls below 0.5 eV at about 4 ms due to the insufficient loss mechanism. The chemical kinetics of oxygen includes multiple types of more effective recombination processes compared to that of argon, causing a considerable difference in the electron decay rates.

Table 2 shows the percentage of the wall loss in the net loss rate of certain species within the considered discharges. The wall flux often forms a significant portion of the net loss in both cylindrical and coaxial structures. For the dominant ions, it reaches up to 98% for Ar$^+$ and up to 58% for O$_2^+$. Among the neutrals, the wall flux also considerably contributes to the net loss for O, O$_2$(a$^3\Delta_g$) and O$_2$(b$^3\Sigma_g^+$) with a maximum value of 56%. The wall loss rates of Ar(4s) and Ar(4p) are negligible, and hence, the simulations are not sensitive to the wall de-excitation probabilities of the excited argon species.

Although the O wall recombination is an important loss mechanism, the recombination probability has only a weak effect on the simulations for a range of 0.009–1. Because of this and due to lack of data, a recombination probability

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**Figure 2.** The measurements performed on distinct coaxial structures of IV [15] and V—see table 1—and the simulation results (line) for a feeding gas of argon. The simulation results are volume-averaged and they are comparable to the spatially-averaged measurements. (a) Radially-resolved electron density (▲) and temperature (■) measurements on the discharge setup IV. The radial averages of the electron density and temperature measurements are denoted by ▲ and ■ respectively. We note the role of the uncontrollable self-pulsing of the power supply in setup IV that is accounted by the effective continuous wave electron temperature in the measurements [15]. (b) Radially-resolved electron density (▲) and temperature (■) measurements as well as their radial averages (denoted by ▲ and ■ respectively) on the setup V. (c) Axially-resolved electron density (▲) and temperature (■) measurements as well as their axial averages (denoted by ▲ and ■ respectively) on the setup V. The measurements are conducted at a radial position of 28 mm. We note that the measurements at a different radial position would change the axial average.

**Figure 3.** The measurements of the discharge setup V—see table 1—and the simulation results (lines). The simulation results are volume-averaged and they are comparable to the spatially-averaged measurements. (a) Radially-resolved electron density (▲) and temperature (■) measurements as well as their radial averages (denoted by ▲ and ■ respectively) on the stationary oxygen plasma. (b) Time-resolved radially-averaged electron density (▲) and temperature (■) measurements for a pulse-modulated power input in argon. (c) Time-resolved radially-averaged measurements of electron density (▲) and temperature (■) for a pulse-modulated power input in oxygen.
Table 2. The percentage of the wall loss rate—either equations (26) for the cylindrical or equations (27) for the coaxial structures—in the net loss rate of dominant ions and certain neutrals. Here, we only consider the discharges operated with continuous power input and refer to table 1 for the corresponding operation parameters. We show the calculation results of setup I at a power input of 107 W and at a pressure of 133 Pa.

| Argon species | (I) | (IV) | (V) | Oxygen species | (II) | (V) |
|---------------|-----|------|-----|----------------|------|-----|
| Ar\(^+\)      | 48  | 32   | 98  | O\(_2\)        | 08  | 58  |
| Ar(4sr)       | 4 \times 10^{-3} | 3 \times 10^{-3} | 3 \times 10^{-2} | O  | 10  | 38  |
| Ar(4p)        | 4 \times 10^{-4} | 4 \times 10^{-5} | 4 \times 10^{-4} | O_2(d\Delta p) | 25  | 29  |
|                |     |      |     | O_2(4p\Sigma\_g^+) | 07  | 56  |

identical to that of the quartz wall is assumed at the entire radial boundaries of the coaxial structure V. Such a weak effect of the recombination probability is in contrast with the observations at low-pressure oxygen plasma [19] that we also confirm with the same chemical kinetics of the current study [25]. The wall recombination is incomparably the most dominant mechanism both in the loss of oxygen atom and the production of the molecular oxygen at low pressure. However, in the relatively higher pressure regime considered, ozone kinetics also have a significant contribution to the oxygen atom loss and to the molecular oxygen production. These reactions substantially suppress the critical role of the wall recombination probability on the surface-wave discharges.

We observe that the considered oxygen discharges are attachment dominated with \( \tau_{\text{att}} \approx K_\infty \gg 20 \), hence the negative ions are not in Boltzmann equilibrium. On the other hand, the simulation results are not sensitive to the resultant variation in the Bohm velocity. The negative ion loss mechanism is dominated by the detachment as expected in the considered pressure regime [40]. A hypothetical inclusion of an axial ion edge-to-centre ratio with the critical edge electron density of the surface-wave propagation [13] are negligible on the results.

The analytically estimated radial Bessel profile is also proposed earlier in cylindrical argon [16] and oxygen discharges of opposite asymptotic \( P \) limits [38, 50, 51]. The former should be disturbed in setup I due to molecular-assisted recombination in the considered case of operation conditions. A Bessel radial distribution in coaxial argon discharge is also observed [15], however, the profile transforms to a similar Gaussian-like shape as the molecular-assisted recombination dominates over the diffusion loss. The simulation results suggest that the molecular-assisted recombination dominates in setup IV, whereas the diffusive wall loss dominates in setup V. The measurements of coaxial argon and oxygen discharges suggest a profile peak closer to the inner wall compared to the corresponding analytically estimated radial Bessel profiles since the power density is localized near the inner wall.

The ion edge-to-centre ratio is numerically comparable with the low-collisionality analogue (\( h^+_{IR} = 3.90 \times 10^{-3} \) and \( \tilde{h}^+_{IR} = 3.88 \times 10^{-3} \)) in argon surfatron (I). The simulations show that the volume and wall losses equally contribute to the net ion loss rate for the plasma, in agreement with the classification by Jimenez-Diaz et al [16]. The value of the neutral edge-to-centre ratio is also similar with the earlier derivation for the excited argon species (\( h_{IR}^+ = 1.73 \times 10^{-3} \) and \( \tilde{h}^+_{IR} = 2.50 \times 10^{-3} \)). The difference in the numerical values is due to the factor of \( (2/2.405)^2 \) and the addition of the axial walls are negligible on the numerical difference. The interchange of the ion and the neutral edge-to-centre ratios with the earlier analogues are negligible on the simulation results.

The numerical values of the ion edge-to-centre ratios significantly differ in the case of oxygen surfatron (II) due to the single electronegative region flat-topped term \( h^+_{IR,C} \). The ratio \( h^+_{IR} \) is higher than \( h^+_{IR,C} \) mostly by a factor of about 10 for a volume loss dominated positive ions within a range of degree of the electronegativity 2–5. The interchange of the ratio with \( \tilde{h}^+_{IR} \) in the simulations reduces a variety of particle densities and raises the electron temperature. This also changes the dominant positive ion loss mechanism to the diffusive wall losses and increases the degree of electronegativity to the range 4–7. The numerical density values are still in the same order and the usage of any edge-to-centre ratios do not lead better agreement with the considered measurements. Compared with the earlier assumption of about 0.05 in the edge-to-volume-averaged formalism [18], the derived edge-to-centre ratio is smaller by a factor of about 0.17. A factor of difference between the edge-to-centre and edge-to-volume-averaged formalisms is about 0.5. The neutral edge-to-centre ratios \( h^N_{IR} \) and \( \tilde{h}^N_{IR} \) are similar in their numerical values and their interchange with each other is not effective on the simulation results. The difference between the ion edge-to-centre ratios is even larger in setup III. The ratio \( h^+_{IR} \) is larger than \( \tilde{h}^+_{IR} \) by a factor of about 200 for \( \alpha \approx 12 \). However, the positive ions are volume loss dominated and the interchange of the edge-to-centre ratios do not significantly alter the simulation results.

4.2. The coaxial setup V

In this section, we analyse the influence of power and pressure on the coaxial discharge V (see table 1 for details) for a feeding gas of either argon or oxygen. The power transfer
efficiency $\beta$ decays with the input power in the range given in table 1, whereas the gas temperature linearly increases. The experiments show that the plasma dimensions do not vary within the considered parameter ranges and the filamentary structures are absent.

The electron density and temperature of the argon plasma are shown in figure 4 as functions of pressure and input power. The electron density increases both for an increasing pressure and power. Since the power transfer efficiency $\beta$ decays with the input power [15], absorbed and input powers do not linearly depend on each other. Therefore, the rate of change of the electron density with respect to the input power decreases as the input power increases. The electron temperature follows a similar trend to that of electron density with respect to the input power, but it features relatively small change. Unlike the electron density, the temperature shows a decay as pressure value rises. The simulations show that the electron density and temperature are equal to their peak values in the pulse-modulated operations in the previous section. The molecular ion density is negligibly small and it increases with pressure. The direct ionization is the dominant ionization channel and the stepwise ionization forms less than 3% of the net ionization rate. The wall flux dominates the loss mechanisms in the considered parameter ranges, forming about 98% of the net ion loss rate. Inner to outer ion wall flux ratio is about 0.4 and the flux density at the inner wall is slightly larger.

Variations of plasma quantities with respect to pressure and input power are shown in figure 5 for a feeding gas of oxygen. The figure includes (a) the electron density and temperature, (b) various ion and (c) neutral densities, (d) the degree of electronegativity $\alpha = (n_O^- + n_O^+ + n_O^2)/n_e$, degree of dissociation $\kappa = n_O^2/(n_O + 2n_O^2)$ and density ratio $a = n_{O(O^2\Delta_g)}/n_{O^2}$.

Figure 5. Various plasma quantities with respect to variations of input power and pressure in the coaxial structure V for a feeding gas of oxygen. (a) The electron density and temperature, (b) ion and (c) neutral concentrations, (d) degree of electronegativity $\alpha = (n_O^- + n_O^+ + n_O^2)/n_e$, degree of dissociation $\kappa = n_O^2/(n_O + 2n_O^2)$ and density ratio $a = n_{O(O^2\Delta_g)}/n_{O^2}$. 

- Efficiency $\beta$ decays with the input power in the range given in table 1, whereas the gas temperature linearly increases.
- The electron density and temperature of the argon plasma are shown in figure 4 as functions of pressure and input power. The electron density increases both for an increasing pressure and power.
- Since the power transfer efficiency $\beta$ decays with the input power [15], absorbed and input powers do not linearly depend on each other. Therefore, the rate of change of the electron density with respect to the input power decreases as the input power increases. The electron temperature follows a similar trend to that of electron density with respect to the input power, but it features relatively small change.
- Unlike the electron density, the temperature shows a decay as pressure value rises. The simulations show that the electron density and temperature are equal to their peak values in the pulse-modulated operations in the previous section.
- The molecular ion density is negligibly small and it increases with pressure. The direct ionization is the dominant ionization channel and the stepwise ionization forms less than 3% of the net ionization rate.
- The wall flux dominates the loss mechanisms in the considered parameter ranges, forming about 98% of the net ion loss rate. Inner to outer ion wall flux ratio is about 0.4 and the flux density at the inner wall is slightly larger.

- Variations of plasma quantities with respect to pressure and input power are shown in figure 5 for a feeding gas of oxygen. The figure includes (a) the electron density and temperature, (b) various ion and (c) neutral densities, (d) the degree of electronegativity $\alpha = (n_O^- + n_O^+ + n_O^2)/n_e$, degree of dissociation $\kappa = n_O^2/(n_O + 2n_O^2)$ and density ratio $a = n_{O(O^2\Delta_g)}/n_{O^2}$. Although, they differ in the rates of growth or decay, the electron density and temperature both show a similar behaviour with the variation of pressure and input power. Both the electron density and temperature decrease with the increase of pressure whereas they increase with the increase of input power. Similar to the argon discharge, the power transfer efficiency $\beta$ induces relatively smaller electron density variation with input power as the power grows.
- The dominant positive and negative ions in the considered parameter ranges are $O_2$ and $O^-$, respectively. However, the rest of the ions, such as, $O^+$ and $O_3^-$, still have considerable concentrations at narrower parameter ranges. Figure 5(b) shows that the most of the charged particles follow a similar trend with pressure and input power, decreasing with the increase of pressure and increasing with the increase of input power. The concentration of $O_3^-$ significantly differs from these charged particles, for which the variation with power is more apparent above 30 Pa. The calculations in section 4.1 show that $O_3^-$ density is comparable to that of the dominant negative ion $O^-$.
the dominance of $O^-$ are also suggested in earlier calculations of a glow discharge by Dettmer [59].

Figure 5(c) shows the densities of various neutral species with the variation of input power and pressure. The most of the neutral concentrations in the figure rise with the increase of the pressure and decrease with the increase of the power. An exception to this behaviour is the slight growth of $O$ density with the rise of the input power. The highest rate of change belongs to the O$_2$ that possesses relatively low values of concentration. Similar neutral density variations with the pressure and the power are also observed by a kinetic model of a cylindrical discharge [60]. Compared to the coaxial structure, much larger ozone concentrations appear in cylindrical discharges II and III. The variation of the degrees of dissociation $\kappa$ and electronegativity $\alpha$ as well as the density ratio $a = n_{O_2}/n_{O_3}$ are shown in figure 5(d). The degree of dissociation reveals the influence of the O$_2$ density, since the variation of O is rather small. The role of the O$_3$ on the degree of electronegativity is apparent at 0.6 kW and vanishes at 1.5 kW. The degree of electronegativity is always less than one in the pressure and power ranges explored. The density ratio $a = n_{O_2}/n_{O_3}$ decreases as the pressure increases and its value varies between 0.07–0.2. Similar density ratio values are also observed in cylindrical discharge II at 133.3 Pa.

Direct electron impact ionization (reaction 1—oxygen reactions start in table B2 in appendix B.) constitutes about 90% of the net O$_2^+$ production rate and the rest of the contribution mostly belongs to ion charge exchange (reaction 34). The main loss mechanism of O$_2^+$ is the wall flux, about 70% of the net loss rate at 15 Pa; and 10% of the loss rate is due to electron-ion recombination (reaction 30) also at 15 Pa. The contribution of the wall flux on the net loss rate decreases with the increase of pressure, down to 25% of the net loss rate at 80 Pa, with inner to outer ion wall flux ratio of about 0.4. At 80 Pa, the wall flux is comparable to electron-ion recombination (reaction 30). The influence of less important loss channels via various ion-recombination reactions strengthens as the pressure increases.

The dominant negative ion $O^-$ is mainly produced by electron attachment (reactions 3 and 4) and lost by detachment (reaction 54). Charge exchange of $O^-$ with O$_3$ (reaction 46) is the main formation channel of O$_3$. Therefore, the variation of O$_3$ density directly influences the O$_3^-$ concentration. The main production mechanism of O$_3$ is reaction 75 that single-handedly dominates the net production rate at 80 Pa. Since O$_2$ is a reactant in reaction 75, the amount of O$_3$ increase in the plasma as pressure increases. Associative detachment (reaction 43) also significantly contributes to O$_3$ production as pressure decreases. Its contribution at 15 Pa even exceeds that of reaction 75 at a large input power of 1.5 kW. The wall recombination dominates the O loss mechanisms at low pressure, forming 50% of the net loss rate at 15 Pa with an inner to outer wall flux ratio of 0.25. At the same pressure value, 30% of the net loss rate belongs to electron impact excitation (reaction 13) and less than 10% belongs to reaction 75. However, the contribution of reaction 75 on the net loss rate increases with the increase of pressure and dominates the loss mechanisms. At a pressure of 80 Pa, it reaches up to 45% at an input power of 1.5 kW and 70% at an input power of 0.6 kW. Electron impact excitation dominates the production and destruction of O$_2(d\Delta_g)$ by reactions 14 and 17, respectively.

5. Conclusions and discussion

A volume-averaged global model is developed for the surface-wave discharges of cylindrical and coaxial structures for both the electropositive and the electronegative plasmas. A set of edge-to-centre density ratios for the neutrals and the positive ions are derived based on an analytical one-dimensional model in order to estimate regarding wall loss rates. The analytical model of charged species is based on the three-component plasma with an assumption of constant or piecewise constant degree of electronegativity as suggested by a variety of earlier studies [11, 20, 39] in the considered collisionality regime. The simulation results are compared with different types of measurements in a wide range of pressure and power and a good agreement is obtained in argon or oxygen surface-wave discharges of cylindrical and coaxial structures for both continuous and pulse-modulated power input. A numerical comparison is made between the derived edge-to-centre ratios in the cylindrical structure and their analogues that are used in the low-pressure plasmas. A difference is observed only in the electronegative oxygen plasma, where the validity of the low-pressure analogue is expired [39, 40, 54].

The percentage of the wall flux on the net loss rates of individual species widely varies in different discharge setups, contributing 8–98% of the positive ion loss and 0–56% of the neutral loss. The recombination of oxygen atoms at the wall is an important mechanism in the considered pressure regime, however, ozone chemical kinetics suppresses its critical role. The analysis of the coaxial discharge (V) reveals the variation of various plasma quantities with respect to input power and pressure. The wall flux is an essential loss channel and its role on the oxygen plasma considerably decays with the increase of pressure. Despite relatively low ozone concentrations, ozone chemical kinetics is influential on the plasma. The calculations suggest more effective influence of the ozone kinetics on the considered cylindrical discharges, containing larger ozone concentrations.

The inhomogeneity in the discharge is often significantly localized, for example, inside the surfatron launcher, near the dielectric surface. However, a homogeneity assumption with a zeroth order degree of homogeneity still holds in the volume-averaged quantities within the numerical range of the model sensitivity. Estimated edge-to-centre ratios sufficiently describe the wall flux rates for an experimentally confirmed volume-averaged particle densities within the sensitivity of the model. The power transfer efficiency of the coaxial discharge of interest (V) is only estimated ignoring the small portion of the axial length with a smaller outer radius. A more accurate estimation can be acquired by coupling the microwave propagation with an appropriate spatially-resolved plasma model. The chemical sets are adopted
from earlier studies in literature and a throughout analysis of the reaction mechanisms is still required for further accuracy. The plasma length and the gas temperature are not calculated in the model and obtained from already available data for each simulation. An incorporation of an analytic model for the surface-wave propagation and an implementation of the volume-averaged heavy-particle energy continuity equation are still necessary for their self-consistent determination.

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Appendix A. Derivation of ion edge-to-centre ratios

The general solution of the ions is earlier given in the form

\[ n_i(r) = C_j_b(\chi r/R) + C_2_f(\chi r/R), \]

where the boundary conditions and the normalization of the maximum entropy define the special—dimensionless—form. At any Bohm point \( r_B \) that is in the vicinity of the corresponding radial plasma wall \( R \), the ions satisfy

\[ -D_i \left( \frac{dn_i}{dr} \right) = (\pm) u_{iBE} n_i, \]

where \( r_B \) corresponds to either the single radial Bohm point of the cylindrical \( R = R \) or double radial Bohm points of the coaxial structure \( R = R \) and only the inner wall \( R = R \) incorporates the negative sign (-) on the right-hand side. We refer to equation (14), for an explicit dependence of \( u_{iBE} \) on the electropositive Bohm velocity \( u_B \). The edge-to-centre ratio at any radial wall is [45]

\[ h_{iE} = \frac{1}{1 + \alpha (u_{iBE}/u_B) n_i}, \]

where the centre value—corresponds to the maximum value for the coaxial structure—is unity via normalisation, \( 1/1 + \alpha \) is an additional factor of normalization in the electronegative discharges [19] and \( (u_{iBE}/u_B) \) is the effect of the electronegativity on the Bohm velocity. Assuming negligibly small sheath length, \( r_B - R \ll R \), the Taylor series expansion at \( R \) leads

\[ \left( \frac{dn_i}{dr} \right)_{r_n} \approx \left( \frac{dn_i}{dr} \right)_{r_B}. \]

Hence, using this with equation (A.2), \( n_i \), can be approximated by the following relation

\[ n_i \approx \left( \frac{\chi D_i + C_f(\chi R^2/R) + C_2_f(\chi R^2/R)}{R u_{iBE}} \right)^{-1/2}. \]

However, it is observed that the edge-to-centre ratios via this approximation often cause computationally unstable simulations. A numerically equivalent and computationally more stable alternative can be estimated from this approximation in the following form

\[ n_i \approx \left( 1 + \left( \frac{R u_{iBE}}{\chi D_i + C_f(\chi R^2/R) + C_2_f(\chi R^2/R)} \right) \right)^{-1/2}. \]

For the sake of computational stability, we prefer the latter form with the edge-to-centre ratio

\[ h_{iE} \approx \frac{1}{1 + \alpha (u_{iBE}/u_B)} \times \left( 1 + \left( \frac{R u_{iBE}}{\chi D_i + C_f(\chi R^2/R) + C_2_f(\chi R^2/R)} \right) \right)^{-1/2}. \]

Appendix B. Chemical kinetics

Chemical sets by Gudmundsson et al [21] are adopted in argon plasma simulations as well as argon excimer reactions and three body recombination by Jimenez et al [16] and Kabouzi et al [56]. The sets for argon are given in figure B1, tables B1, B5 and B6. A previously adopted species and reaction sets are used in the oxygen simulations without a reduction [18]. The sets for oxygen are given in figure B1, tables B2, B3, B4, B5 and B6.
Table B1. Argon plasma reactions. We adopt the chemical set by Gudmundsson et al [21] and additionally include the argon excimer ion kinetics as well as three-body recombination by Jimenez et al [16] or Kabouzi et al [56]. The electron impact reaction rates are calculated assuming a Maxwellian electron energy distribution and they are valid in the range 1–7 eV. The units of the rate coefficients are m³ s⁻¹ and those of electron and gas temperatures are eV and K, respectively, if not stated otherwise.

| # | Reaction | Rate Coefficient | Reference |
|---|----------|------------------|-----------|
| 1 | e + Ar → Ar⁺ + 2e | 2.3 × 10⁻¹² T_e^0.59 e⁻¹⁷.⁴⁴/T_e | [61] |
| 2 | e + Ar → e + Ar(4s_n) | 5.0 × 10⁻¹⁵ e⁻¹².⁶⁴/T_e | [62] |
| 3 | e + Ar → e + Ar(4s_u) | 1.4 × 10⁻¹¹ e⁻¹².²²/T_e | [62] |
| 4 | e + Ar → e + Ar(4s) | 1.9 × 10⁻¹⁵ e⁻¹².⁶⁰/T_e | [62] |
| 5 | e + Ar → e + Ar(4s) | 2.7 × 10⁻¹⁵ e⁻¹².¹⁴/T_e | [62] |
| 6 | e + Ar → e + Ar(4p) | 2.1 × 10⁻¹⁴ e⁻¹³.¹³/T_e | [63] |
| 7 | e + Ar(4s_n) → e + Ar | 4.3 × 10⁻¹⁶ T_e⁰.⁷⁴ | [64] |
| 8 | e + Ar(4s_n) → Ar⁺ + 2e | 6.8 × 10⁻¹⁵ T_e⁰.⁶⁷ e⁻².²⁰/T_e | [65] |
| 9 | e + Ar(4s_u) → e + Ar(4s_u) | 3.7 × 10⁻¹³ | [66] |
| 10 | e + Ar(4s_n) → e + Ar(4p) | 8.9 × 10⁻¹⁵ T_e⁰.⁵¹ e⁻¹.⁵⁹/T_e | [65] |
| 11 | 2Ar(4s_n) → 2Ar | 2.0 × 10⁻¹³ | [21] |
| 12 | Ar + Ar⁺ → Ar + Ar⁺ | 2.2 × 10⁻¹⁶ | [67] |
| 13 | Ar(4s_n) + Ar(4s) → Ar + Ar⁺ + e | 2.1 × 10⁻¹⁵ | [68] |
| 14 | Ar(4p) + Ar(4p) → Ar + Ar⁺ + e | 5.0 × 10⁻¹⁶ | [65] |
| 15 | Ar(4s_n) + Ar(4s_u) → Ar + Ar⁺ + e | 6.4 × 10⁻¹⁶ | [66] |
| 16 | e + Ar(4p) → Ar⁺ + 2e | 1.8 × 10⁻¹⁷ T_e⁰.⁶⁴ e⁻².⁶¹/T_e | [65] |
| 17 | e + Ar(4p) → Ar(4s) + e | 3.0 × 10⁻¹⁷ T_e⁰.⁵¹ | [64] |
| 18 | e + Ar(4p) → Ar(4s_n) + e | 3.0 × 10⁻¹⁷ T_e⁰.⁵¹ | [64] |
| 19 | e + Ar(4p) → Ar + e | 3.9 × 10⁻¹⁷ T_e⁰.⁷¹ | [64] |
| 20 | Ar + Ar(4s_n) → 2Ar | 2.1 × 10⁻²¹ | [68] |
| 21 | e + Ar(4s) → Ar + e | 4.3 × 10⁻¹⁶ T_e⁰.⁷⁴ | [64] |
| 22 | e + Ar(4s) → Ar(4s_n) + e | 9.1 × 10⁻¹³ | [66] |
| 23 | e + Ar(4s) → Ar(4p) + e | 8.9 × 10⁻¹⁵ T_e⁰.⁵¹ e⁻¹.⁵⁹/T_e | [65] |
| 24 | Ar(4s) → Ar | 1.0 × 10⁰⁵ [1 s⁻¹] | [69] |
| 25 | Ar(4p) → Ar | 3.2 × 10⁰⁷ [1 s⁻¹] | [64] |
| 26 | Ar(4p) → Ar(4s_n) | 3.0 × 10⁰⁷ [1 s⁻¹] | [70] |
| 27 | Ar(4p) → Ar(4s_u) | 3.0 × 10⁰⁷ [1 s⁻¹] | [70] |
| 28 | Ar⁺ + e → Ar(4s_n) + Ar | 1.0 × 10⁻¹²(T_e (K)/300)^⁻⁰.⁶⁷(1 – e⁻¹⁴.¹⁸/T_e)/(1 – 0.31 e⁻¹⁴.¹⁸/T_e) | [56] |
| 29 | Ar⁺ + e → Ar(4s_u) + Ar | 1.0 × 10⁻¹²(T_e (K)/300)^⁻⁰.⁶⁷(1 – e⁻¹⁴.¹⁸/T_e)/(1 – 0.31 e⁻¹⁴.¹⁸/T_e) | [56] |
| 30 | Ar⁺ + e → Ar⁺ + Ar + e | 1.1 × 10⁻¹² e⁻².⁹⁴–⁰.³⁶/T_e (eV) e⁻⁻⁰.⁰⁵/T_e | [56] |
| 31 | Ar⁺ + 2Ar → Ar⁺ + Ar | 2.25 × 10⁻⁴(T_e/300)^⁻⁰.⁴ (m² s⁻¹) | [56] |
| 32 | Ar⁺ + Ar → Ar⁺ + 2Ar | 5.22 × 10⁻⁶(T_e (eV))⁻¹.⁴⁰/T_e e⁻⁻¹.³⁰⁴/T_e (eV) | [56] |
| 33 | Ar⁺ + 2e → Ar(4p) + e | 5.00 × 10⁻⁹(T_e)^⁻⁴.⁵ (m² s⁻¹) | [71] |
| 34 | Ar⁺ + 2e → Ar + e | 8.75 × 10⁻⁹ T_e⁻².²⁵ (m² s⁻¹) | [72] |
| #  | Reaction                        | Rate Coefficient                           | Reference |
|----|--------------------------------|---------------------------------------------|-----------|
| 1  | \( e + O_2 \rightarrow O_2 + 2e \) | \( 2.01 \times 10^{-15} T_e^{-0.09} \) | [73]      |
| 2  | \( e + O_2 \rightarrow O(3P) + O^+ + 2e \) | \( 1.04 \times 10^{-14} T_e^{1.11} \) | [73]      |
| 3  | \( e + O_2 \rightarrow O(3P) + O^- \) | \( 1.12 \times 10^{-15} T_e^{-1.41} \) | [74]      |
| 4  | \( e + O_2(a^3\Delta_g) \rightarrow O(3P) + O^- \) | \( 4.33 \times 10^{-15} T_e^{-1.39} \) | [74]      |
| 5  | \( e + O_2(a^3\Delta_g) \rightarrow O(3D) + O^- \) | \( 1.01 \times 10^{-15} T_e^{-1.46} \) | [74]      |
| 6  | \( e + O_2(A^3\Sigma_u^+, ...) \rightarrow O(3P) + O^- \) | \( 5.77 \times 10^{-16} T_e^{-0.90} \) | [75]      |
| 7  | \( e + O(3P) \rightarrow O^+ + 2e \) | \( 4.75 \times 10^{-15} T_e^{0.78} \) | [76]      |
| 8  | \( e + O^- \rightarrow O(3P) + 2e \) | \( 4.64 \times 10^{-14} T_e^{0.50} \) | [77]      |
| 9  | \( e + O_2 \rightarrow O(3P) + O(3D) + e \) | \( 8.45 \times 10^{-15} T_e^{0.38} \) | [78]      |
| 10 | \( e + O_2 \rightarrow O(3P) + O(3D) + e \) | \( 9.49 \times 10^{-16} T_e^{0.38} \) | [78]      |
| 11 | \( e + O_2 \rightarrow O(3D) + O(3D) + e \) | \( 9.49 \times 10^{-17} T_e^{0.38} \) | [78]      |
| 12 | \( e + O_2 \rightarrow O^+ + O^- + e \) | \( 4.12 \times 10^{-14} T_e^{-0.25} \) | [79]      |
| 13 | \( e + O(3P) \rightarrow O(3D) + e \) | \( 2.19 \times 10^{-14} T_e^{0.57} \) | [80]      |
| 14 | \( e + O_2 \rightarrow O_2(a^3\Delta_g) + e \) | \( 1.25 \times 10^{-14} T_e^{-0.97} \) | [81]      |
| 15 | \( e + O_2 \rightarrow O_2(b^1\Sigma_u^+, ...) + e \) | \( 3.84 \times 10^{-15} T_e^{1.05} \) | [81]      |
| 16 | \( e + O_2 \rightarrow O_2(A^3\Sigma_u^+, ...) + e \) | \( 2.39 \times 10^{-14} T_e^{1.00} \) | [82]      |
| 17 | \( e + O_2(a^3\Delta_g) \rightarrow O_2(b^1\Sigma_u^+) + e \) | \( 6.69 \times 10^{-15} T_e^{0.56} \) | [83]      |
| 18 | \( e + O_2(a^3\Delta_g) \rightarrow O_2(A^3\Sigma_u^+, ...) + e \) | \( 7.23 \times 10^{-14} T_e^{1.25} \) | [83]      |
| 19 | \( e + O_2(b^1\Sigma_u^+) \rightarrow O_2(A^3\Sigma_u^+, ...) + e \) | \( 8.47 \times 10^{-14} T_e^{1.21} \) | [83]      |
| 20 | \( e + O_2 \rightarrow O_2 + O^- \) | \( 3.24 \times 10^{-15} T_e^{0.94} \) | [84]      |
| 21 | \( e + O_3 \rightarrow O(3P) + O_2 \) | \( 9.56 \times 10^{-16} T_e^{0.26} \) | [84]      |
| 22 | \( e + O_3 \rightarrow O_2 + O(3P) + e \) | \( 1.42 \times 10^{-14} T_e^{0.68} \) | [85]      |
| 23 | \( e + O_3 \rightarrow O_2(a^3\Delta_g) + O(3P) + e \) | \( 4.16 \times 10^{-15} T_e^{-0.73} \) | [85]      |
| 24 | \( e + O_3 \rightarrow O_2(a^3\Delta_g) + O(3D) + e \) | \( 6.68 \times 10^{-15} T_e^{0.82} \) | [85]      |
| 25 | \( e + O_3 \rightarrow O_2(b^1\Sigma_u^+) + O(3D) + e \) | \( 1.34 \times 10^{-13} T_e^{0.87} \) | [85]      |
| 26 | \( e + O_2 \rightarrow O_2 + 2e \) | \( 5.74 \times 10^{-14} T_e^{0.55} \) | [86]      |
| 27 | \( e + O_3 \rightarrow O_3 + 2e \) | \( 3.43 \times 10^{-14} T_e^{0.33} \) | [87]      |
| 28 | \( e + O_3 \rightarrow O_2 + O(3P) + 2e \) | \( 2.69 \times 10^{-14} T_e^{0.66} \) | [87]      |
| 29 | \( e + O_3 \rightarrow O_2 + O^- + e \) | \( 3.67 \times 10^{-14} T_e^{-0.10} \) | [87]      |
| 30 | \( e + O_2 \rightarrow O(3P) + O(3D) \) | \( 2.20 \times 10^{-14} T_e^{0.50} \) | [88]      |

Table B2. Electron—Oxygen reactions [18]. The rate coefficients are given in m³ s⁻¹ and the electron temperature is given in eV. The symbol ‘*’ is used to specify the inverse reaction coefficients calculated by detailed balancing.
### Table B3. Oxygen-Oxygen reactions [18]. The rate coefficients and the gas temperature are given in m$^3$ s$^{-1}$ and K, respectively. An exception is the rate coefficient of reaction 68 with a unit of 1 s$^{-1}$.

| #  | Reaction                                                                 | Rate Coefficient                  | Reference |
|----|-------------------------------------------------------------------------|-----------------------------------|-----------|
| 31 | O$_2^+$ + O$^-$ $\rightarrow$ O$_2$ + O($^3P$)                          | $2.60 \times 10^{-14} (300/T)$    | [88]      |
| 32 | O$_2^+$ + O$^-$ $\rightarrow$ 2O($^3P$)                                 | $4.00 \times 10^{-14} (300/T)$    | [88]      |
| 33 | O($^3P$) + O$^-$ $\rightarrow$ O$_2$ + e                                | $2.30 \times 10^{-16}$            |           |
| 34 | O$_2^+$ + O$^-$ $\rightarrow$ O($^1P$) + O$_2^+$                         | $2.10 \times 10^{-17} (300/T)$    | [90]      |
| 35 | O$_2^+$ + O($^1D$) $\rightarrow$ O$_2$ + O($^3P$)                       | $2.56 \times 10^{-13} e^{300/T}$  | [90]      |
| 36 | O($^3P$) + O($^1D$) $\rightarrow$ 2O($^3P$)                            | $8.00 \times 10^{-18}$            |           |
| 37 | O$_2$($^2\Delta_g$) + O$^-$ $\rightarrow$ O($^1P$) + O$_2$             | $4.75 \times 10^{-17}$            | [89]      |
| 38 | O$_2^+$ + O$_2$ $\rightarrow$ 2O$_2$                                    | $2.01 \times 10^{-13} (300/T)$    | [90]      |
| 39 | O$_2^+$ + O$_2$ $\rightarrow$ O$_2$ + O($^3P$)                          | $2.70 \times 10^{-13} (300/T)$    | [90]      |
| 40 | O($^3P$) + O$_2$ $\rightarrow$ O$_2$ + O$^-$                           | $3.31 \times 10^{-16}$            |           |
| 41 | O$_2$($^2\Delta_g$) + O$_2$ $\rightarrow$ 2O$_2$ + e                   | $2.00 \times 10^{-16}$            | [92]      |
| 42 | O$_2$ + O$^-$ $\rightarrow$ O$_3$ + e                                   | $5.00 \times 10^{-21}$            |           |
| 43 | O$_2$($^2\Delta_g$) + O$^-$ $\rightarrow$ O$_3$ + e                    | $1.42 \times 10^{-16}$            | [89]      |
| 44 | O$_2$ + O$^-$ $\rightarrow$ O$_2$ + O$_2^+$                            | $1.00 \times 10^{-16}$            |           |
| 45 | O($^3P$) + O$_2$ $\rightarrow$ 2O$_2$                                   | $1.81 \times 10^{-17} e^{-300/T}$ |           |
| 46 | O$_2$ + O$^-$ $\rightarrow$ O($^1P$) + O$_2$                           | $5.30 \times 10^{-16}$            |           |
| 47 | O($^3P$) + O$_2$ $\rightarrow$ O$_2$ + O$_2$                           | $1.00 \times 10^{-16}$            |           |
| 48 | O($^3P$) + O$_2$ $\rightarrow$ O$_2$ + O$^+$                            | $3.00 \times 10^{-16}$            |           |
| 49 | O$_2^+$ + O$_2$ $\rightarrow$ O$_2$ + O$_3$                             | $2.00 \times 10^{-13} (300/T)$    | [90]      |
| 50 | O$_2^+$ + O$_2$ $\rightarrow$ 2O($^3P$) + O$_3$                         | $1.01 \times 10^{-13} (300/T)$    | [90]      |
| 51 | O$_2$ + O$_2$ $\rightarrow$ O$_2$ + O$_3$                              | $4.00 \times 10^{-16}$            |           |
| 52 | O($^3P$) + O$_2$ $\rightarrow$ O$_2$ + O$_3$                            | $3.30 \times 10^{-16}$            |           |
| 53 | O$_2$ + O($^1D$) $\rightarrow$ O$_2$($^2\Delta_g$) + O($^1P$)          | $1.00 \times 10^{-18}$            |           |
| 54 | O$_2$($^3P$) + O$^-$ $\rightarrow$ O$_2$ + O($^1P$) + e                | $6.90 \times 10^{-16}$            |           |
| 55 | O$_2$($^3P$) + O$^-$ $\rightarrow$ O$_2$ + O($^3P$) + O($^1P$)          | $8.10 \times 10^{-20}$            |           |
| 56 | O$_2$ + O$_2$($^3P$) $\rightarrow$ O$_2$ + O$_2$($^3P$)                | $3.79 \times 10^{-22} e^{-281/T}$ |           |
| 57 | O$_2$($^2\Delta_g$) + O($^3P$) $\rightarrow$ O$_2$ + O($^3P$)          | $1.30 \times 10^{-22}$            |           |
| 58 | O$_2^+$ + O$^-$ $\rightarrow$ 3O($^3P$)                                 | $2.60 \times 10^{-14} (300/T)$    | [88]      |
| 59 | O$_2$ + O$_2$($^2\Delta_g$) $\rightarrow$ 2O$_2$                       | $2.20 \times 10^{-23} (300/T)$    | [88]      |
| 60 | O$_2$($^3P$) + O$^-$ $\rightarrow$ O$_2$($^3P$) + O$^-$                | $1.35 \times 10^{-18}$            |           |
| 61 | O$_2$ + O$_2$ $\rightarrow$ 2O$_2$ + O($^3P$)                           | $7.26 \times 10^{-16} e^{-1400/T}$|           |
| 62 | O$_2$($^3P$) + O$_2$($^3P$) $\rightarrow$ O$_2$ + O$_2$($^3P$)          | $1.80 \times 10^{-23} (300/T)$    | [98]      |
| 63 | O$_2$($^2\Delta_g$) + O$_2$($^2\Delta_g$) $\rightarrow$ 2O$_2$         | $5.50 \times 10^{-23} (300/T)$    | [98]      |
| 64 | O$_2$($^3P$) + O$_2$($^3P$) $\rightarrow$ O$_2$ + O($^3P$)             | $1.50 \times 10^{-17}$            |           |
| 65 | O$_2$($^2\Delta_g$) + O$_2$($^2\Delta_g$) $\rightarrow$ O$_2$ + O($^3P$) | $6.01 \times 10^{-17} e^{-2853/T}$|           |
| 66 | O$_2$ + O$_2$($^3P$) $\rightarrow$ 2O$_2$ + O($^3P$)                    | $2.90 \times 10^{-19}$            |           |
| 67 | O$_2$ + O$_2$($^3P$) $\rightarrow$ 2O$_2$ + O($^3P$)                    | $1.01 \times 10^{-14} (300/T)$    |           |
| 68 | O$_2$($^3P$) + O$_2$($^3P$) $\rightarrow$ O$_2$ + O$_2$($^3P$)          | $6.25 [1 \text{ s}^{-1}]$         |           |
| 69 | O$_2$($^3P$) + O$_2$($^3P$) $\rightarrow$ O$_2$ + O($^3P$)              | $4.95 \times 10^{-18}$            |           |
| 70 | O$_2$($^3P$) + O$_2$($^3P$) $\rightarrow$ O$_2$($^3P$) + O($^3P$)       | $2.70 \times 10^{-18}$            |           |
| 71 | 2O$_2$($^3P$) + O$_2$($^2\Delta_g$) $\rightarrow$ O$_2$ + O$_2$($^2\Delta_g$) | $3.60 \times 10^{-23} (300/T)$    | [103]     |
### Table B4. Three body reactions [18]. The rate coefficients and the gas temperature are given in m$^{6}$ s$^{-1}$ and K, respectively, whereas the electron temperature is in eV.

| # | Reaction | Rate Coefficient | Reference |
|---|----------|------------------|-----------|
| 72 | $e + e + O^{+} \rightarrow O(3P) + e$ | $7.89 \times 10^{-30} T^{4.50}$ | [90] |
| 73 | $e + O_{2} + O_{2} \rightarrow O_{2} + O_{2}$ | $2.26 \times 10^{-42} T^{0.50}$ | [104] |
| 74 | $O + O + O_{2} \rightarrow O + O_{2}$ | $6.3 \times 10^{-46}(300/T_{e})^{2}$ | [105] |
| 75 | $O + O(3P) + O(3P) \rightarrow O(3P) + O_{2}$ | $2.15 \times 10^{-46} e^{345/T_{e}}$ | [32] |
| 76 | $e + O_{2} + O(3P) \rightarrow O_{2} + O^{+}$ | $1.00 \times 10^{-43}$ | [90] |
| 77 | $e + O_{2} + O(3P) \rightarrow O_{2} + O^{+}$ | $1.00 \times 10^{-43}$ | [90] |
| 78 | $O + O^{+} \rightarrow O_{2} + O(3P)$ | $1.00 \times 10^{-28}$ | [90] |
| 79 | $O + O^{+} \rightarrow O_{2} + O^{+}$ | $1.00 \times 10^{-32}(300/T_{e})$ | [90] |
| 80 | $O + O^{+} \rightarrow O_{2} + O_{2}$ | $2.10 \times 10^{-37}(300/T_{e})^{2.50}$ | [90] |
| 81 | $O_{2} + O^{+} \rightarrow O_{2} + O_{2}$ | $2.01 \times 10^{-37}(300/T_{e})^{2.50}$ | [90] |
| 82 | $O_{2} + O^{+} \rightarrow O_{2} + O_{2}$ | $6.90 \times 10^{-46}(300/T_{e})^{2.25}$ | [90] |
| 83 | $O_{2} + O(3P) + O(3P) \rightarrow O_{2} + O_{2}(A^{3} \Sigma_{u}^{+}, ...)$ | $1.20 \times 10^{-46}$ | [101] |
| 84 | $O_{2} + O_{2}(A^{3} \Delta_{g}) + O(3P) \rightarrow O_{2} + O_{2} + O(3P)$ | $1.00 \times 10^{-44}$ | [97] |
| 85 | $3O_{2}(3P) \rightarrow O_{2}(a^{3} \Delta_{g}) + O(3P)$ | $1.93 \times 10^{-47}(300/T_{e})^{0.63}$ | [95] |
| 86 | $O_{2} + O(3P) + O(3P) \rightarrow O_{2} + O_{2}(a^{3} \Delta_{g})$ | $6.93 \times 10^{-47}(300/T_{e})^{0.63}$ | [95] |

### Table B5. Elastic electronic collisions included in the simulations.

| # | Collision | Reference |
|---|-----------|-----------|
| 1 | $e + Ar$ | [106] |
| 2 | $e + O_{2}$ | [107] |
| 3 | $e + O$ | [108] |
| 4 | $e + O_{3}$ | [85] |

### Table B6. Chemical reactions induced at the wall.

| # | Reaction | Probability($\gamma$) $R_p$ | Probability($\gamma$) $R$ | Reference |
|---|----------|-----------------------------|-----------------------------|-----------|
| 1 | Ar(4s, 4p) + wall $\rightarrow$ Ar | 1 | 1 | [16] |
| 2 | O($^{3}P$, $^{1}D$) + wall $\rightarrow$ 1/2O$_{2}$ | 0.09 | 0.09(a) | [109] |
| 3 | O($^{3}P$) + wall $\rightarrow$ O($^{3}P$) | 0.1 | 0.1 | [32] |
| 4 | O$_{2}(a^{3} \Sigma_{u}^{+})$ + wall $\rightarrow$ O$_{2}$ | 0.007 | 0.007 | [110] |
| 5 | O$_{2}(b^{3} \Sigma_{g}^{+})$ + wall $\rightarrow$ O$_{2}$ | 0.1 | 0.1 | [32] |
| 6 | O$_{2}(a^{3} \Sigma_{u}^{+}, ...)$ + wall $\rightarrow$ O$_{2}$ | 0.1 | 0.1 | [32] |

(a) We include a wall recombination value of 0.001 in setup III (see [18, 43] for further details).

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