Electrical Characteristics, Plasma parameters and Reaction Rates of DC O₂ Plasma

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The electrical characteristics of DC oxygen(O₂) plasma such as the discharge current-voltage (I-V) curves and the breakdown voltage of oxygen gas were measured. The plasma parameters such as electron temperature (T_e) and density (n_e) were obtained using Langmuir probe at a constant power over a wide rangeof O₂ gas pressures. The measured T_e values were used to calculate the various rate coefficients for electron impact (ionization, dissociation and excitation) from ground state of O₂ molecules. Thereafter, the calculated rate coefficients and the measured $n_e$values were used to calculate the rates of ionization, dissociation and excitation from ground state of O₂ molecules. The I-V measurements of the discharge and Paschen curve show that the operating voltage decreased with increasing O₂ gas pressures at constant current and the minimum of Paschen curve was found to be 400 V at Pd = 1.86 mbar.cm, respectively. The $T_e$showed a decreasing trend with increasing O₂ gas pressures while n_e showed an increasing trend. The rate coefficients of ionization, dissociation and excitation were found to decrease with increasing O₂ gas pressure. On the contrary, the rates of ionization, dissociation and excitation were found to increase with increasing O₂ gas pressure.

Keywords: *DC plasma / Electron temperature / Electron density / Rate coefficients / Ionization and dissociation rates*

Introduction

Low pressure oxygen plasmas have been used in the field of plasma processing for decades with different applications such as ashing of photoresist [1], oxidation or thin film oxides deposition and removing organic polymide films [2,3].Oxygen discharge plasmas have also been used in the sterilization processes (e.g. bacteria inactivation) and improving surface properties of polymeric materials [4,5]. Low pressure oxygen discharge plasma is an electronegative plasma consisting of free electrons, positive ions, and negative ions, which were produced by the electron attachment to the neutral atoms or molecules [6]. Low pressure oxygen discharge plasma can be generated using several types of energy sources such as microwave (MW), radiofrequency (RF) and direct high voltage (DC HV). Although the plasma density produced by applying RF and MW as energy source is higher than that produced by applying of DC HV.The DC plasma has several advantages compared to the other energy sources. It doesnot require a matching unit and it is of the lowest cost. Moreover, the DC plasma reactors have the advantages of low maintenance cost and simple operation. Depending on the operating voltage and current the DC plasma are divided into several types such as the Townsend or dark, glow and arc discharges [7].

Oxygen plasmas contain several reactive species such as metastable oxygen molecules O₂ ($a^1\Delta_g$, b $^1\Sigma_g^+$), O_2^+ and oxygen atoms O (^3P, ^1D), which renders it the best in many applications [8]. The previous reactive species are produced due to

ionization, excitation and dissociation processes of neutral species in these plasmas. Therefore, it is necessary to study and understand the rate coefficients and rates of the processes responsible for the production of these active species. The electron temperature is an important parameter for understanding the rate coefficients of ionization, excitation and dissociation in oxygen plasmas.

In the present work, DC O_2 plasmas system was characterized. The electrical characteristics of the system such as the breakdown voltage in terms of Paschen curve and the I-V curves were evaluated and discussed in detail. The single Langmuir probe was used to determine plasma parameters, such as electron temperature (T_e) and electron density (n_e). The rate coefficients of the most important processes occurring in oxygen plasmas were evaluated using the values of electron temperature (T_e),then, the values of rate coefficients are used in the evaluation of rate of electron impact ionization, dissociation and excitation.

Material and Method
A schematic diagram of the DC oxygen plasma experimental set up is shown in Fig.(1). The set-up of the system includes the following components. Plasma chamber, DC power supply, Vacuum system and Langmuir single probe. The plasma chamber is made of a Pyrex glass cylinder of 13 cm inner diameter and 20 cm in length. Two parallel movable stainless-steel discsof 100 mm diameter acted as discharge electrodes. The inter-electrode separation is adjusted to be 70 mm. The low pressure in the plasma chamber is achieved by using a rotary pump (*Edwards H. vacuum pump, model ED 200*) which can evacuate the chamber pressure down to 0.0013 mbar. The flow of O_2 is monitored with mass flow controller and enters the plasma chamber via controllable needle valve whereas the working pressure in the plasma chamber is monitored by using pirani gauge. The low pressure O_2 plasmas is ignited by DC power supply which can produce discharge voltage up to 2 K V.

In order to get the required data for plotting the breakdown (Paschen) curves, the inter-electrode separation was fixed at 70 mm while the working gas pressure was adjusted from 0.053 to 1.33 mbar. On the other hand, the I-V characteristic curves of the discharge are obtained by varying the potential difference between the two electrodes and recording the corresponding current in the pressure range from 0.133 to 1.33 mbar. Finally, the internal plasma parameters such as T_e and n_e, which are required to understand the rate coefficients of ionization, excitation and dissociation in oxygen plasmas were obtained by using single Langmuir probe. The Langmuir probe is a Tungsten wire enclosed in a Pyrex glass tube. The probe tip is of 0.03 cm diameter and 0.5 cm length. The I-V characteristics of single Langmuir Probe were plotted by recording the probe current for a DC bias voltages ranging from −50 to +50 V.
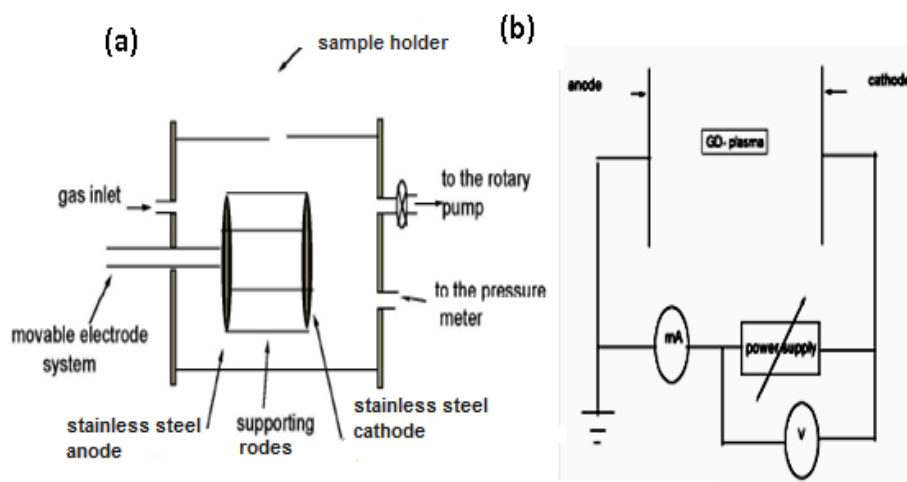
Fig. (1): A schematic diagram for (a) The experimental equipment and (b) The electrical circuit

Results and Discussion

Electrical Characteristics

The dependence of the breakdown voltage (V_B) on the product of working gas pressure (P) and the inter electrode separation (d) is usually represented by a Paschen curve. The measurements of breakdown voltage values were determined as a function of (Pd), where inter electrode separation was fixed at 7 cm and the O_2 gas pressure varied from 0.053 to 1.33 mbar and the results are shown in Fig.(2). The Pd parameter is a scaling parameter proportional to the frequency of electron-neutral collisions over unit distance. Accordingly, atypical sudden increase of V_B at low Pd-s can be attributed to the small number of electron-neutral oscillation frequencyFig.(2). On the other hand, at high Pd-s V_B is increased slowly due to a large number of electron-neutral oscillation frequency. There is a minimum value between low and high Pd-s, at which the generation of charges by electron impact ionization and secondary electron emission mechanisms and losses by drift, diffusion and attachment are balanced [9]. Our minimum breakdown voltage is 400 V at Pd = 1.86 (mbar.cm) and this value in agreement with reported by Khalaf et al. [10].

The current-volt (I-V) characteristic curves at different working pressures of O_2gas are shown in Fig.(3). From this figure It can be noticed that as the applied voltage increase, the discharge current increase at the same O_2gas pressure.Moreover, it is clearly seen that at the same discharge current, the applied voltage decreases with increasing the O_2gas pressure. At a discharge current of 3 mA, the applied voltage decreases from 702 V to 450 V as the O_2gas pressure increases from 0.133 to 1.33 mbar. In other words, plasma electrical conductivity increases by increasing the O_2 gas pressure. In plasma, both ions and electrons are carrying the electrical plasma current. The plasma electrical conductivity is given by the microscopic plasma parameters [11]:

$$\sigma = \frac{e^2 n_e}{m_e \nu}$$

Where e and m_e are the electron electric charge and mass, respectively, n_e is the plasma electron number density and ν is the frequency of collisions between electrons and neutral atoms or molecules in plasma.

With increasing the O_2 gas pressure in the plasma chamber the electron number density is increased. This is also observed from the single Langmuir probe measurements which will be shown later. The behavior of applied voltage with O_2 gas pressure at constant discharge current is similar to that reported by K. Yasserian et al. and O. F. Farag [12,13].
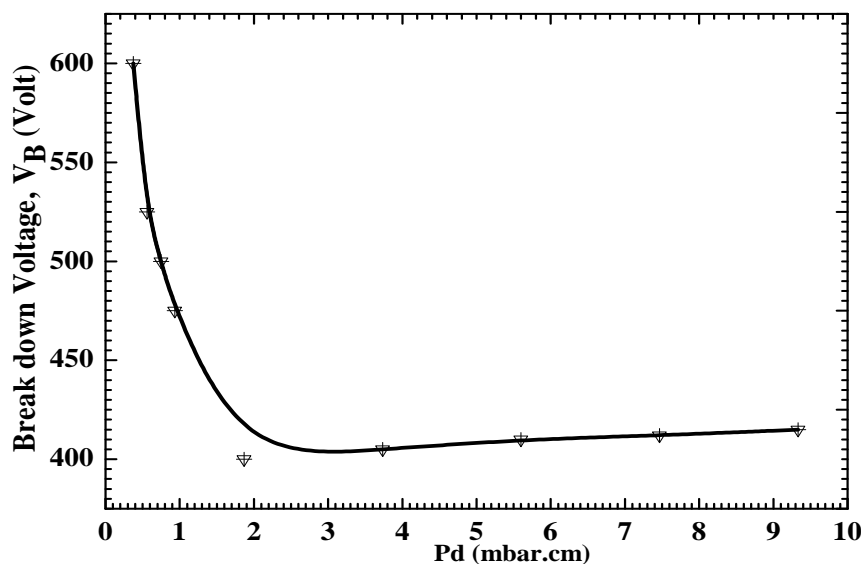

Figure (2): Paschen curve show the variation of V_B with the product Pd of O_2 at d = 7cm

Plasma Parameters

The electron temperature, T_e, and electron number density, n_e, are calculated from single Langmuir probe I-V characteristic curve by using the appropriate expressions as shown in Mansour et al. (2013) and Farag and Mansour (2013) [14,15]. The influence of working gas pressure on T_e and n_e was discussed in detail. First, the influence of working gas pressure on the T_e and n_e was investigated while the power of O_2 discharge is adjusted at about 3.5 W. As illustrated in Fig.(4), T_e decreases with the increase in O_2 gas pressure inside the plasma chamber at a constant discharge power. This is in contrast to the behavior of n_e, which increased with increasing O_2 gas pressure. The values of T_e and n_e are about 6.69 eV and 0.7258×10^9 cm^{-3} at O_2 gas pressure and applied power are about 0.133 mbar and 3.5 W, respectively. As the O_2 gas pressure increases to 1.06 mbar and the applied power remains constant, T_e decreases to 4.27 eV and n_e increases to 5.304×10^9 cm^{-3} as shown in Fig. (4). The behavior of T_e and n_e with O_2 gas pressure is consistent with that reported by Gudmundsson et al. (2000) [16].
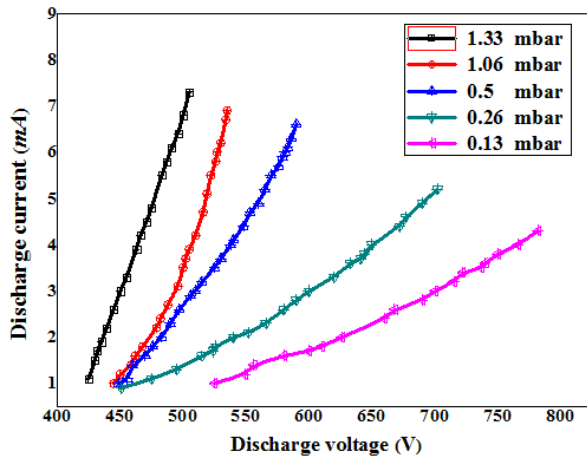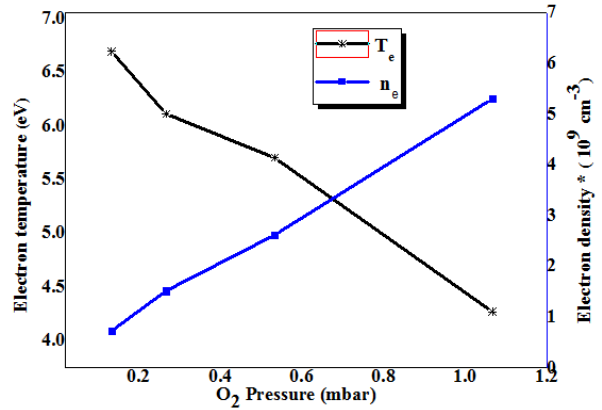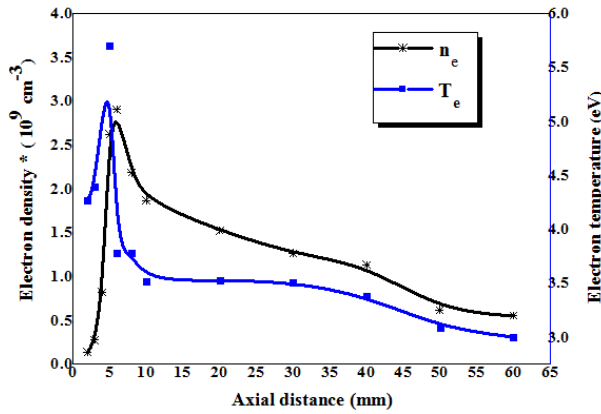

Figure (4): Electron (temperature and density) variation with O_2gas pressure at discharge power 3.5 W

The axial profile of T_e and n_e for oxygen discharge at operating conditions of O_2 gas pressure = 0.5 mbar and applied power about 3.5 W is shown in Figure 5. The value of T_e is highest at the edge of the cathode fall region (CF). This may be attributed to two reasons, first the high electric field and second, the absence of inelastic collisions between the accelerated electrons with oxygen molecules and/or atoms in this region. Beyond the CF region, the value of T_e drops through the negative glow region (where the electric field drops in this region and many ionization and excitation collisions occur) and becomes nearly constant throughout the whole region to the anode (also this could be attributed to the very weak electric field). From Figure 5 the axial profile of n_e can be described as, the value of n_e is the lowest in the CF region and in the negative glow region it reached maximum value. Moreover, the values of n_e are nearly constant through the negative glow region and near the anode region dropping slightly. The axial profiles of T_e and n_e are similar to that reported by Farag (2010) [13].

Figure (3): The I-V characteristic curves of O_2 at different working pressures (chamber pressure) at distance 7cm

Figure (5): Axial distribution of electron (temperature and density) of DC O₂ plasma at gas pressure 0.5 of mbar and at a discharge power of 3.5 W

Rate

In the present study, it is assumed that the formation of active oxygen plasma species such as O_2 ($a^1\Delta_g$, $b^1\Sigma_g^+$), O_2^+ and oxygen atoms O (^{3}P, ^{1}D) are resulting from direct electron impact to ground state oxygen molecules. The rate coefficients for the production of the previous active oxygen plasma species by electron impact collisions were calculated assuming the electron energy distribution is Maxwellian and fit over the electron temperature in the range 1-7 V [16]. According to Gudmundsson [17] the rate coefficients for electron impact ionization,

dissociation and excitation for oxygen molecules in terms of electron temperature T_e are given in Table (1).

The ionization rate coefficient, K_{iz}, due to direct electron impact to O_2 in the ground state as a function of O_2 gas pressure, is shown in Fig. (6-a). As can be seen from the figure, an increase in the O_2 pressure results in a noticeable influence on the ionization rate. As the O_2 gas pressure increases the ionization rate coefficient shows a decreasing trend due to the inverse relationship between gas pressure and the electron temperature.

Dissociation rate coefficients, K_{diss}^1, K_{diss}^2 and K_{diss}^3, due to the reactions (R2,R3 and R4) for O_2 plasma as a function of O_2 gas pressure are illustrated in Fig. (6-b). The dissociation rate coefficients due to the three reactions showed a decreasing trend with increasing O2 gas pressure. This also could be attributed to the inverse relationship between gas pressure and electron temperature. The dissociation rate coefficient due to reaction R3, K_{diss}^2 is about five orders of magnitude higher than that due to reaction R2, K_{diss}^1. The dissociation rate coefficient due to reaction R4, K_{diss}^3 is the lowest one and the dissociation due it is of less importance.

Table (1): Electron impact ionization, dissociation and excitation rate coefficients of oxygen molecules

Reaction	Rate coefficient (m³ S⁻¹)
(R1) $e + O_2 \rightarrow O_2^+ + 2e$	$k_{iz} = 2.34\times10^{-15} T_e^{1.03} \exp(-12.29/T_e)$
(R2) $e + O_2 \rightarrow O_2(A^3\Sigma_u^+, A'^3\Delta_u, c^1\Sigma_u^- \rightarrow O(^3P) + O(^3P) + e$	$k_{diss}^1 = 6.86\times10^{-15} \exp(-6.29/T_e)$
(R3) $e + O_2 \rightarrow O_2(B^3\Sigma_u^-, B'^3\Sigma_u^-, 2^3\Pi_u) \rightarrow O(^3P) + O(^1D) + e$	$k_{diss}^2 = 3.49\times10^{-14} \exp(-5.92/T_e)$
(R4) $e + O_2 \rightarrow O(^1D) + O(^1D) + e$	$k_{diss}^3 = 1.44\times10^{-16} \exp(-17.25/T_e)$
(R5) $e + O_2(X^3\Sigma_g^-) \rightarrow O_2(a^1\Delta_g) + e$	$k_{ex}^{delta} = 1.37\times10^{-15} \exp(-2.14/T_e)$
(R6) $e + O_2(X^3\Sigma_g^-) \rightarrow O_2(b^1\Sigma_g^+) + e$	$k_{ex}^{sigma} = 3.24\times10^{-16} \exp(-2.218/T_e)$

The excitation rate coefficients of metastable oxygen molecule O_2 ($a^1\Delta_g$ and $b^1\Sigma_g^+$) from ground state, K_{ex}^{delta} and K_{ex}^{sigma}, due to the reactions (R5 and R6) for O_2 plasma as a function of O_2 pressure are shown in Fig. (6-c). The excitation rate coefficients, K_{ex}^{delta} and K_{ex}^{sigma}, showed a decreasing trend with increasing O_2 gas pressure. Also, the values of K_{ex}^{delta} are higher than those for K_{ex}^{sigma} at the same electron temperature. This could be attributed to the excitation cross section for the transition for O_2 ($X^3\Sigma_g^-$) $\rightarrow O_2$ ($a^1\Delta_g$) is larger than that for the transition O_2 ($X^3\Sigma_g^-$) $\rightarrow O_2$($b^1\Sigma_g^+$) at the same temperature.

The axial profiles of ionization, dissociation and excitation rate coefficients for oxygen discharge at operating conditions as O_2 gas pressure = 0.5 mbar and applied power about 3.5 W are shown in Fig.(7). The axial profiles of ionization, dissociation and excitation rate coefficients are similar to that of the electron temperature (see Fig. 5). Also, it should be noted that the ionization, dissociation and excitation rate coefficients occur over a large area in the negative glow region comparing to it is in the CF region. These results are in good agreement with those given by Meyyappan and Kreskovesky [18] who concluded that in low pressure DC glow discharges, most of ionization and excitation occur in the negative glow region rather than in the CF region.

The rate production of O_2^+, atoms O (^3P, ^1D) and O_2 ($a^1\Delta_g$, $b^1\Sigma_g^+$) via the ionization, dissociation and excitation reactions, respectively was calculated by the use of the obtained values of rate coefficients (k) and electron number density (n_e) in the above sections according to the following expression [19]:

$$R = n_e n_g k \tag{1}$$

Where n_g is the neutral gas density, is calculated from the pressure and temperature of the gas by using ideal gas law ($n_g = P/K_B T_g$). In the present work, T_g is measured by a thermal couple and is 300 K.

The ionization, dissociation and excitation rates for O_2 plasma as a function of O_2 gas pressure are illustrated in Fig. (8). It can be noticed that the behavior of the three rates with the O_2 pressure is the same where the three rates shown an increasing trend with increasing O_2 gas pressure. According to equation 1, the reaction rate is directly proportional

to the electron number density, the density of the neutral particles and reaction rate coefficient, so with an increasing O_2 gas pressure: n_e and n_g increase and consequently the reaction rate increases while T_e decreases and hence the reaction rate coefficient (k) decreases; consequently, the reaction rate decreases. Based on the present results, the effect of n_e and n_g is more effective than k. Therefore, the rate of the ionization, dissociation and excitation reactions increases by increasing the O_2 gas pressure. The behavior of the reaction rate with the gas pressure is similar to that reported in literature [19, 20].
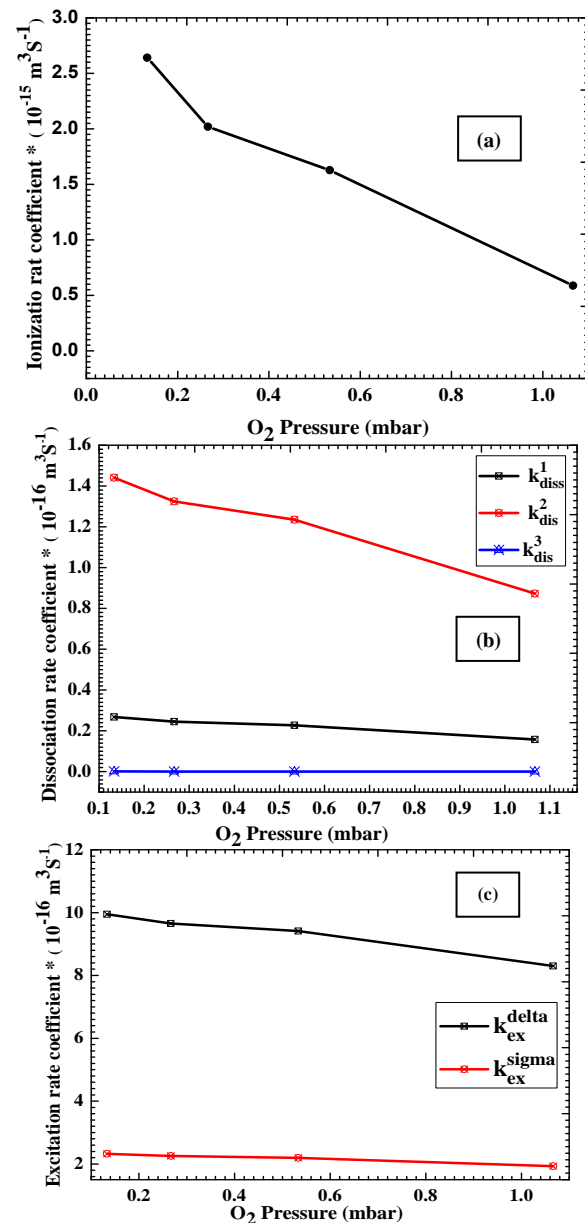

Figure (6): Variation of electron impact (a) ionization, (b) dissociation and (c) excitation rate coefficients with gas pressure in DC O_2 Plasma at discharge power 3.5 W
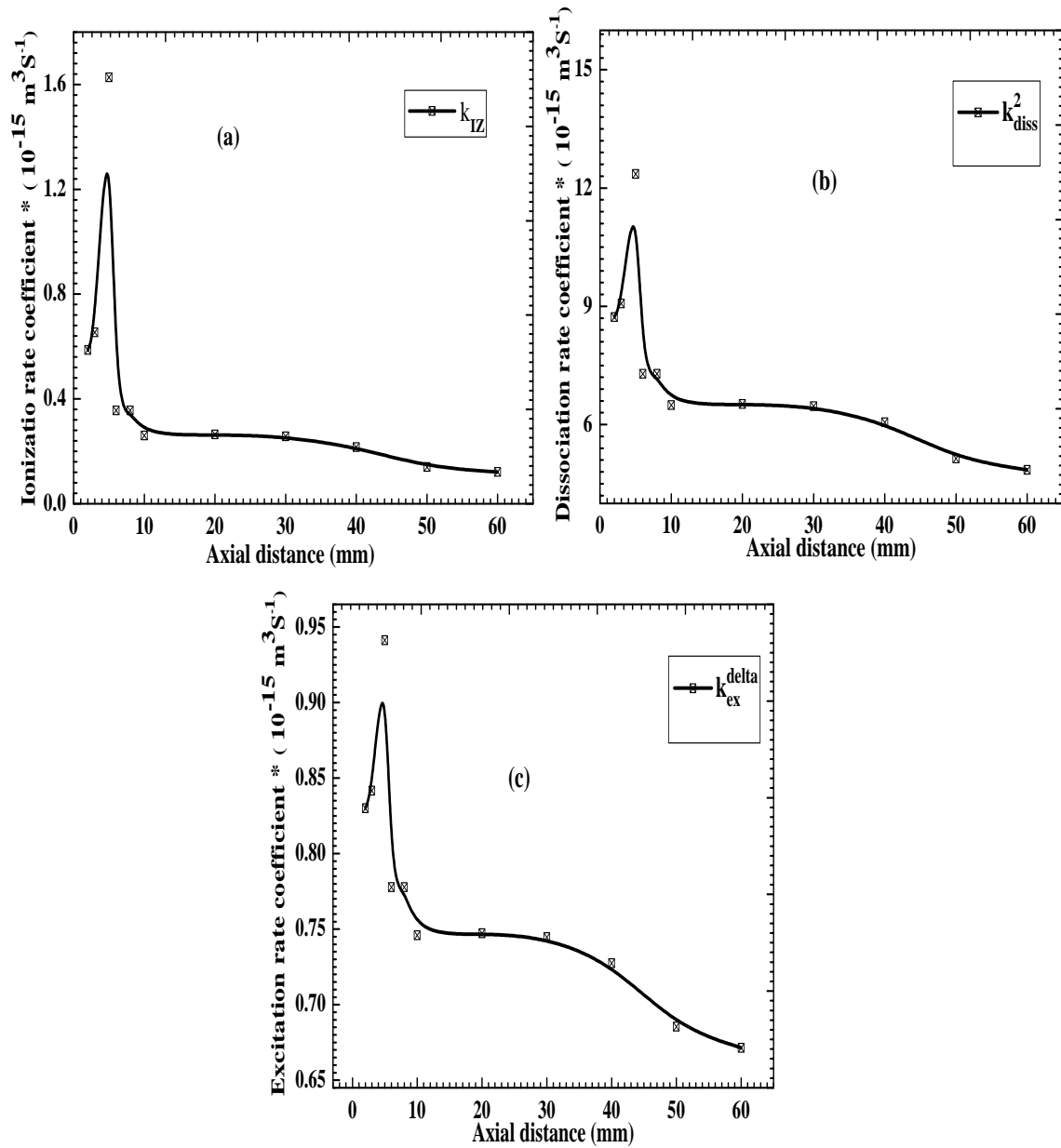
Figure (7): Axial distribution of electron impact (a) ionization, (b) dissociation and (c) excitation rate coefficients in DC O$_2$ Plasma at discharge power 3.5 W and P = 0.5 mbar

The axial profiles of electron impact ionization, dissociation and excitation rates for oxygen discharge at the operating conditions of O_2 gas pressure = 0.5 mbar and applied power about 3.5 W are shown in Fig.(9). The axial profiles of ionization, dissociation and excitation rates are similar to that of the electron number density (see Fig. 5). It should also be noted that the ionization, dissociation and excitation rates occur over a large area in the negative glow region comparing to it is in the CF region.

Conclusion

The electrical characteristics and plasma parameters of DC O_2 plasma at low pressure have been investigated experimentally. The DC glow discharge plasma generated in the present investigation operate in the normal mode where the discharge current is in the range 1 to 10 mA and increases with increasing operating voltage. The breakdown voltage depends on the product of (Pd). The Values of electron temperature (T_e) and density (n_e) which are necessary to calculate the rate coefficients and rates of electron impact ionization, dissociation and excitation have been determined by using the current-voltage characteristic curves of the single Langmuir probe. As the plasma power is constant at 3.5 W, the T_e decreased with increasing O_2 gas pressure while n_e increased with increasing O_2 gas pressure. The rate coefficients of ionization, dissociation and excitation reactions decrease with increasing O_2 gas pressure while their rates increased with increasing O_2 gas pressure. The axial profiles of ionization, dissociation and excitation rate coefficients and rates have maximum at the edge of the negative glow region.
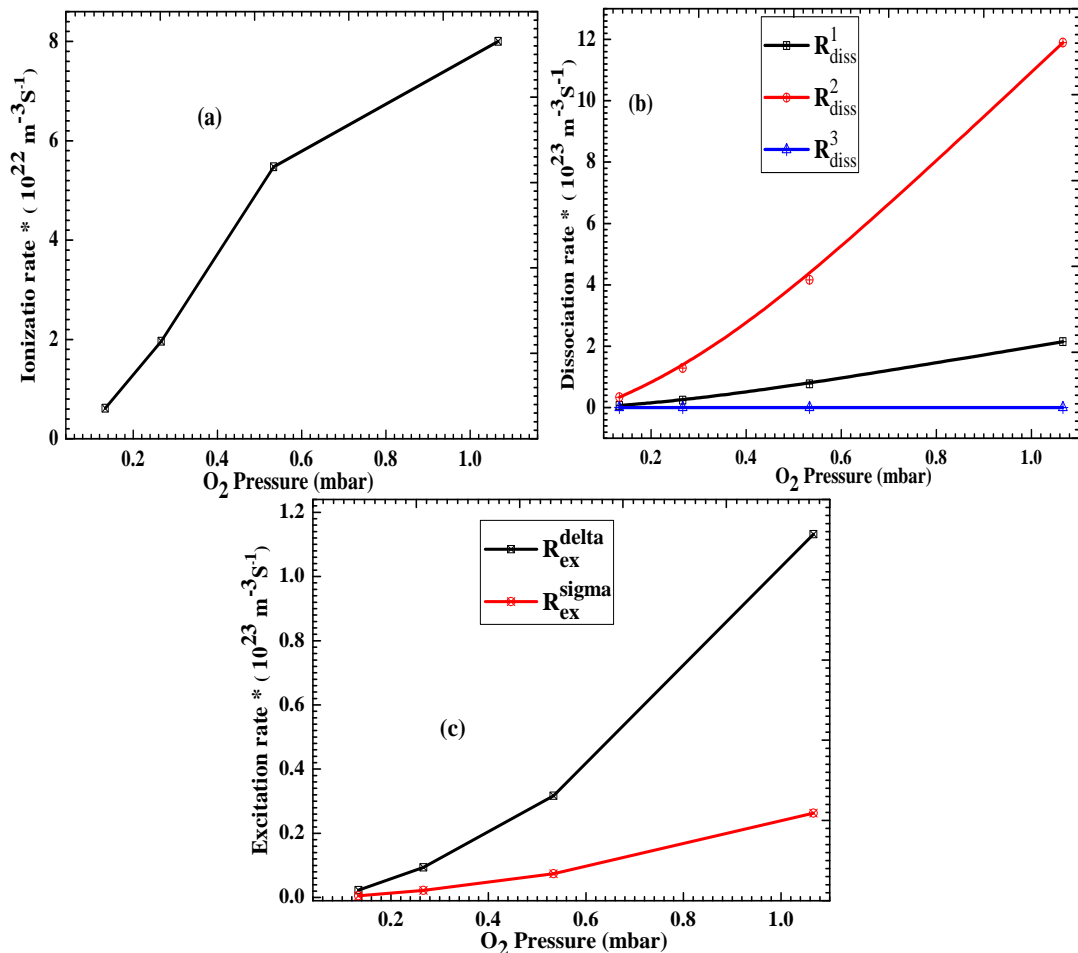

Figure (8): Variation of electron impact (a) ionization, (b) dissociation and (c) excitation rate with gas pressure in DC O_2 Plasma at discharge power 3.5 W
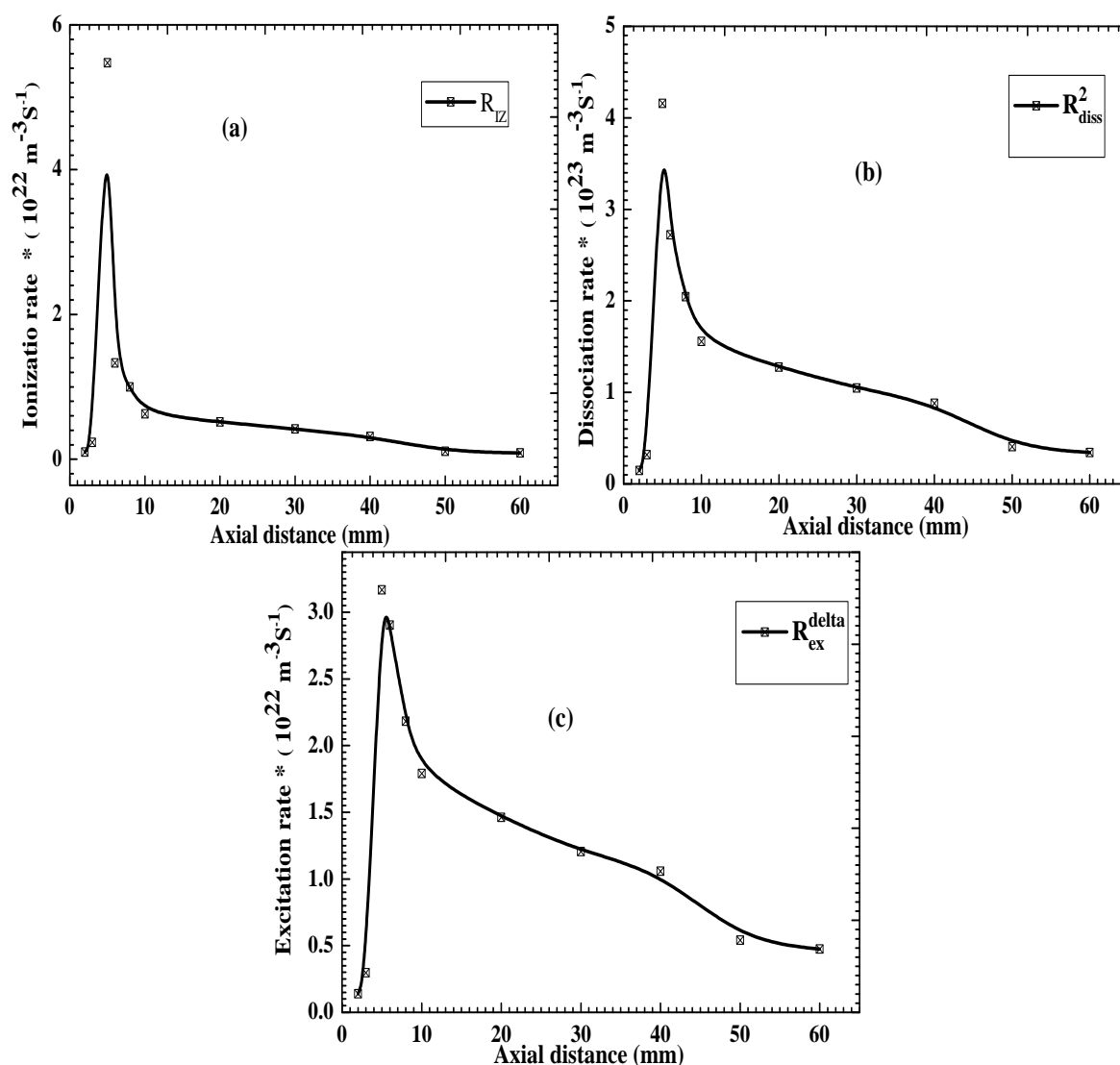
Figure (9): Axial distribution of electron impact (a) ionization, (b) dissociation and (c) excitation rate in DC O_2 Plasma at discharge power 3.5 W and P = 0.5 mbar

References

1- J T Gudmundsson and E G Thorsteinsson, Oxygen discharges diluted with argon: dissociation processes, Plasma Sources Science and Technology, 2007, **16**, 399.

2- D A Carl, D W Hess, M A Lieberman, T D Nguyen and R Gronsky, Effects of dc bias on the kinetics and electrical properties of silicon dioxide grown in an electron cyclotron resonance plasma, Journal of Applied Physics, 1991, **70**, 3301.

3- M Kitajima, H Kuroki, H Shinno and K G Nakamura, Growth of silicon oxide on silicon in the thin film region in an oxygen plasma, Solid State Communications, 1992, **83**, 385.

4- A ABolshakov, B A Gruden, R. Mogul, M V V S Rao, S P Sharama, B N Khare and M Meyyappan,

Radio-frequency oxygen plasma as a sterilization source, AIAA Journal, 2004, **42**, 823.

5- S Modarresi, M Soltanieh, S A Mousavi and I Shabani, Effect of low-frequency oxygen Plasma on Polysulfone membranes for CO_2/CH_4 Separation, Journal of Applied Polymer Science, 2012, **124**, E199.

6- SK Jong andHK Gon, Characterization of an Oxygen Plasma By Using a Langmuir Probe in a Inductively Coupled Plasma, Journal of the Korean Physical Society, 2001, **38**, 259.

7- A Bogaerts, 1996, PhD thesis, University of Antwerp, Belgium.

8- K Kutasi, V Guerra, P A Sa, Active species downstream of an Ar–O_2 surface-wave microwave discharge for biomedicine, surface treatment and

nanostructuring, Plasma Sources Science and Technology, 2011, **20**,035006.

9-D Maric, M Savic, J Sivos, N Skoro, M R Radjenovic, G Malovic, and Z Lj. Petrovi, Gas breakdown and secondary electron yields, European Physical Journal D, 2014, **68**, 1.

10-M K Khalaf, I R Agooi and S H Abd Muslim, Electrical Characteristics and plasma diagnostics of (Ar/O_2) gas mixture glow discharge, International Journal of Application or Innovation in Engineering and management, 2014, **3**, 113.

11-F Araghi and D Dorranian, Effect of negative ions on the characteristics of plasma in a cylindrical discharge, Journal of Theoretical and Applied Physics, 2013, **7:41**, 1-8.

12-K Yasserian, M Ghornneviss, M Aslaninejad, Langmuir probe measurements in a cylindrical magnetron discharge in the presence of Ar/O2, Japanese Journal of Applied Physics, 2009, **48**, 036001.

13-O F Farag, Msc thesis, 2010, Zagazig University, Egypt.

14-M M Mansour, N M El-Sayed, O F Farag and M H Elghazaly; Effect of He and Ar addition on N_2 glow discharge characteristics and plasma diagnostics, Arab Journal of Nuclear Science and Applications, 2013, **46**, 116.

15-M M Mansour and O F Farag, Experimental study of the influence of nitrogen admixture on characteristics of DC glow discharge in He gas, Der ChemicaSinica, 2013, **4**,94.

16-J T Gudmundsson, A M Marakhtanov, K K Patel, V P Gopinath and M A Lieberman, On the plasma parameters of a planar inductive oxygen discharge, Journal of Physics D: Applied Physics, 2000, **33**, 1323.

17-J T Gudmundsson, A critical review of the reaction set for a low pressure oxygen processing discharge, Department of electrical and computer engineering, university of Iceland, Iceland, (2004).

18-M Meyyappan and J P Kreskovesky, Glow discharge simulation through solutions to the moments of the Boltzmann transport equation, Journal of Applied Physics, 1990, **68**, 1506-12.

19-J T Gudmundsson, I G Kouznestov, K K Patel M A Lieberman, Electronegativity of Low-Pressure High-Density Oxygen Discharges, Journal of Physics D: Applied Physics, 2001, **34**, 1100.

20-M H Elghazaly and S Solyman, Electron impact ionization and excitation rate coefficients in the negative glow region of a glow discharge, Journal of Quantitative Spectroscopy and Radiative transfer, 2007, **103**, 260.