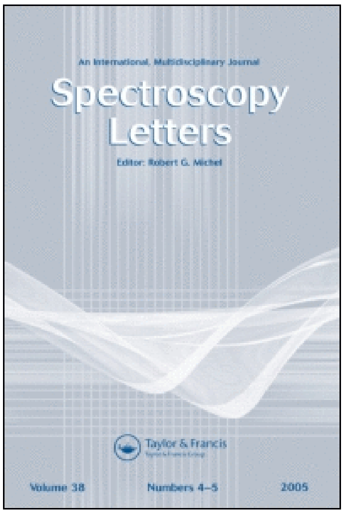

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ENHANCEMENT OF H^- PRODUCTION IN HOLLOW CATHODE DISCHARGE BY USING HYDROGEN AND NEON MIXTURE

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ABSTRACT

The purpose of this study is to find a way for more effective H^- production in hollow cathode glow discharge. It is achieved by using hollow cathode plasma of H_2 and Ne mixture. Based on an appropriate model including the vibrational kinetics a quantitative calculation of H^- concentration in pure H_2 and ($H_2 + 90\%$Ne) hollow cathode discharges is performed. For ($H_2 + 90\%$Ne) mixture the calculated H^-concentration of $3.2 \times 10^8\,\mathrm{cm}^{-3}$ has one order of magnitude higher value than for the pure H_2 hollow cathode discharge. This enhanced H^- concentration in the mixture is due to higher electron concentration giving rise to more effective dissociative attachment of electron to H_2.

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Key Words: Hollow cathode discharge; Hydrogen; Negative ions; Hydrogen plasma kinetics

INTRODUCTION

The concentration of the negative ions is a basic parameter in different plasma sources and its increase is usually achieved by optimization of plasma conditions, by appropriate source design and by insertion of some proper additives into the discharge plasmas.[1,2] The hollow cathode discharge is well known spectral and plasma source containing a great number of various ions including negative ions. Taking into account this fact, the investigation of the negative ions in the hollow cathode plasma is of continuos interest.[3–5]

Our previous investigations showed an increase of the hollow cathode plasma conductivity for $(H_2 + Ne)$ mixtures in comparison with pure H_2 discharge related to the change of the elementary processes with electron participation.[6] In this connection, the aim of the present study is to estimate how this change influences the processes of arising and destruction of H^- in order to obtain more effective H^- production. To reach this aim the electron temperature and concentration are measured for pure H_2 and $(H_2 + 90\%Ne)$ hollow cathode discharges and H^- concentration is theoretically calculated for both cases by using an appropriate kinetic model. The contribution of the processes of arising and destruction of H^- are analyzed on this basis.

THEORETICAL ESTIMATIONS

Our investigations are performed for hollow cathode discharge at 1 Torr discharge pressure and 14 mA discharge current. The Al hollow cathode has 6 mm radius and 40 mm length. The values of electron temperature T_e and electron concentration n_e are measured by using Langmuir's probe. Their values are $T_e = 3.0$ eV, $n_e = 2.0 \times 10^{11}\,cm^{-3}$ and $T_e = 1.7$ eV, $n_e = 5.3 \times 10^{11}\,cm^{-3}$ for pure H_2 and for $(H_2 + 90\%Ne)$ hollow cathode discharges, respectively.

In the calculations the basic elementary processes are considered in which H^-, H, H^+, $H_2{}^+$, Ne^+ and vibrational excited states H_2 (v) participate. The main processes included in the model for these calculations together with their characteristics are shown in Table 1. The k_1–k_7 rate constants are taken from the literature.[7–11] The k_9–k_{11} rate constants are calculated by using the relevent cross-sections[7,8] and the electron energy

Table 1. Elementary Processes and Their Characteristics Included in the Calculations for H_2 and ($H_2 + 90\%$Ne) Hollow Cathode Discharges

	Characteristics of the Process			
Process	H_2 Discharge		($H_2 + 90\%$Ne) Discharge	Ref.
$H^- + H_2 \rightarrow H_2 + H + e$		$k_1 = 4.9 \times 10^{-10}\ cm^3 s^{-1}$		7
$H^- + H \rightarrow H_2 + e$		$k_2 = 1.8 \times 10^{-9}\ cm^3 s^{-1}$		7
$H^- + H_2^+ \rightarrow H + H_2 + e$		$k_3 = 5 \times 10^{-8}\ cm^3 s^{-1}$		8
$H^- + H^+ \rightarrow H + H$		$k_4 = 3.9 \times 10^{-7}\ cm^3 s^{-1}$		8
$H^+ + e \rightarrow H + h\nu$		$k_5 = 1.7 \times 10^{-13}\ cm^3 s^{-1}$		9
$H_2^+ + e \rightarrow H + H$		$k_6 = 3.8 \times 10^{-9}\ cm^3 s^{-1}$		10
$H_2 + e \rightarrow H + H + e$		$k_7 = 5 \times 10^{-12}\ cm^3 s^{-1}$		11
$H_2(v) + e \rightarrow H^- + H$		$k_8(v)$ see Table III		
$H + e \rightarrow H^- + h\nu$	$k_9 = 5.9 \times 10^{-15}\ cm^3 s^{-1}$		$k_9 = 5.2 \times 10^{-15}\ cm^3 s^{-1}$	8
$H^- + e \rightarrow H + 2e$	$k_{10} = 5.8 \times 10^{-9}\ cm^3 s^{-1}$		$k_{10} = 7.6 \times 10^{-9}\ cm^3 s^{-1}$	7
$H^- + Ne^+ \rightarrow Ne^* + H$	—		$k_{11} = 4.6 \times 10^{-7}\ cm^3 s^{-1}$	8
$Ne + e \rightarrow Ne^+ + 2e$	—		$\nu_{12} = 4.7 \times 10^{-1} s^{-1}$	15
$H_2 + e \rightarrow H^+ + H + 2e$	$\nu_{13} = 1 \times 10^{-3}\ s^{-1}$		$\nu_{13} = 1.1 \times 10^{-3}\ s^{-1}$	12
$H_2 + e \rightarrow H_2^+ + 2e$	$\nu_{14} = 4.3 \times 10^{-1}\ s^{-1}$		$\nu_{14} = 4.4 \times 10^{-1} s^{-1}$	13
$H + e \rightarrow H^+ + 2e$	$\nu_{15} = 0.18\ s^{-1}$		$\nu_{15} = 0.19\ s^{-1}$	14
Diffusion H^+	$\tau_{16} = 1.2 \times 10^{-6}$ s		$\tau_{16} = 2.1 \times 10^{-6}$ s	15
Diffusion H_2^+	$\tau_{17} = 1.7 \times 10^{-6}$ s		$\tau_{17} = 2.9 \times 10^{-6}$ s	15
Diffusion Ne^+	—		$\tau_{18} = 1.1 \times 10^{-5}$ s	15

distribution function. Having in mind that this function in hollow cathode glow discharge may be taken to consist of Maxwellian part and electron beam with energies up to the cathode potential fall, the ionization by beam electrons with energy ε can be expressed by

$$\nu = \sigma_{ion}(\varepsilon) j/e, \qquad (1)$$

where ν is the ionization frequency, σ_{ion} is the ionization cross-sections taken from,[12–15] e is the electron charge and $j = 1\,mA/cm^2$ is the discharge current density at the two cases under interest.

The ambipolar diffusion times τ_{16}, τ_{17} and τ_{18} of H^+, $H_2{}^+$ and Ne^+ ions are estimated for our discharge conditions by the following expression

$$\tau = (R/2.4)^2/D, \qquad (2)$$

where D are the diffusion coefficients taken from[15] and R is the cathode radius.

The dissociative attachment and the electron attachment are well known as the main elementary processes for H^- production at low-pressure plasmas. The process of dissociative attachment depends on the vibrationally excited H_2 levels since its cross-section changes by orders of magnitude as a function of $H_2(v)$ states. We have taken into account only $v \geq 4$ since the cross-sections for $v < 4$ have some orders of magnitude lower values.[16] The $H_2(v)$ states are populated by impacts of $H_2(v = 0)$ levels with slow electrons

$$H_2 + e \Rightarrow H_2(v) + e, \qquad (3)$$

and they are mainly depopulated by impacts with electrons (4), impacts between H_2 molecules (5,6) and diffusion to the cathode walls:

$$H_2(v) + e \Rightarrow H_2(w > v) + e, \qquad (4)$$

$$\text{v-v processes} \quad H_2(v) + H_2(v_1) \Rightarrow H_2(v_2 < v) + H_2(w_1 > v_1), \qquad (5)$$

$$\text{v-T processes} \quad H_2(v) + H_2(v_1) \Rightarrow H_2(v_2 < v) + H_2(v_1). \qquad (6)$$

The rate constants for the processes (3,4) calculated by using the cross-sections from [9] are presented in Table 2. The rate constants for the processes (5,6) are taken from.[17,18]

Table 2. Rate Constants for the Processes (3–6) Connected with the Vibrational States of H_2

Rate Constants (cm^3s^{-1})	H_2 Discharge	($H_2 + 90\%$Ne) Discharge
Process (3) k(0,v)		
k(0,4)	7.4×10^{-12}	5.6×10^{-12}
k(0,5)	8.9×10^{-13}	7.1×10^{-13}
k(0,6)	1.2×10^{-13}	9.3×10^{-14}
k(0,7)	1.4×10^{-14}	1.1×10^{-14}
k(0,8)	1.8×10^{-15}	1.4×10^{-15}
k(0,9)	2.2×10^{-16}	1.8×10^{-16}
Process (4) k(v,w)		
k(4,5), k(5,6), k(6,7), k(7,8), k(8,9)	7.4×10^{-9}	6.0×10^{-9}
k(4,6), k(5,7), k(6,8), k(7,9)	9.3×10^{-10}	7.5×10^{-10}
k(4,7), k(5,8), k(6,9)	1.1×10^{-10}	8.9×10^{-11}
k(4,8), k(5,9)	7.4×10^{-12}	5.9×10^{-12}
k(4,9)	8.9×10^{-13}	7.2×10^{-13}

Based on the described processes (3–6) and their rate constants the balance equations for vibrational states of H_2 are written:

$$H_2(v) = \frac{k(0,v)H_2(0)n_e + \sum_{v_2<v} k(v_2,v)H_2(v_2)n_e + K(v+1,v)H_2(0) + K(v+1,v|0,1)H_2(v+1)H_2(0)}{\sum_{w>v} k(v,w)n_e + K(v,v-1)H_2(0) + K(v,v-1|0,1)H_2(0) - \tau_v} \quad (7)$$

where τ_v is the time of free diffusion of $H_2(v)$. It is estimated to be $\tau_v = 8 \times 10^{-5}$ s for the mixture and $\tau_v = 6.3 \times 10^{-5}$ s for pure H_2 discharge by using the expression (2). The populations of $H_2(v = 4–9)$ levels obtained by solving of Eqs. (7) are shown in Table 3.

The concentrations of particles under consideration are obtained by the balance equations (8–12) which are written by using the processes listed in Table 1 and the calculated data in Table 3:

$$H^- = \frac{\sum_{v=4}^{9} k_8 H_2(v) n_e + k_9 H n_e}{k_1 H_2 + k_2 H + k_3 H_2^+ + k_4 H^+ + k_{10} n_e + k_{11} Ne^+} \quad (8)$$

$$Ne^+ = \frac{v_{12} Ne}{(1/\tau_{18} + k_{11} H^-)} \quad (9)$$

Table 3. Calculated Populations of Vibrational Levels $H_2(v)$ and Rate Constants $k_8(v)$ of Dissociative Attachment of H_2

	H_2 Discharge		$(H_2+90\%Ne)$ Discharge	
Vibrational Level v	$k_8(v)$ (cm^3s^{-1})	$H_2(v)$ (cm^{-3})	$k_8(v)$ (cm^3s^{-1})	$H_2(v)$ (cm^{-3})
4	4.5×10^{-10}	8.1×10^{11}	6.0×10^{-10}	5.3×10^{11}
5	1.5×10^{-9}	1.2×10^{11}	2.0×10^{-9}	1.5×10^{11}
6	3.4×10^{-9}	1.8×10^{10}	5.0×10^{-9}	4.5×10^{10}
7	4.5×10^{-9}	2.7×10^{9}	7.2×10^{-9}	1.3×10^{10}
8	2.8×10^{-9}	2.9×10^{8}	5.0×10^{-9}	2.2×10^{9}
9	3.1×10^{-9}	7.6×10^{7}	5.8×10^{-9}	8.7×10^{8}

$$H^+ = \frac{v_{13}H_2 + v_{15}H}{k_4H^- + k_5n_e + 1/\tau_{16}} \tag{10}$$

$$H_2^+ = \frac{v_{14}H_2}{k_3H^- + k_6n_e + 1/\tau_{17}} \tag{11}$$

$$H = \frac{\sum_{v=4}^{9} k_8H_2(v)n_e + H^-\left[k_1H_2 + k_3H_2^+ + 2k_4H^+ + k_{10}n_e + k_{11}Ne^+\right] + H_2[v_{13} + 2k_7n_e] + k_5n_eH^+ + 2k_6n_eH_2^+}{k_2H^- + k_9n_e + v_{15}} \tag{12}$$

where H^-, Ne^+, H^+, $H_2{}^+$ are the negative and positive ion concentrations and Ne, H and H_2 are neon atom, hydrogen atom and hydrogen molecule concentrations, respectively. The system of Eqs. (8–12) is solved for both pure H_2 and (H_2+Ne) hollow cathode plasmas and the results obtained are presented in Table 4. It is seen that the calculated H^- concentration has one order of magnitude higher value in $(H_2+90\%Ne)$ mixture than in pure H_2 hollow cathode discharge.

DISCUSSION AND CONCLUSION

The theoretical model described above allows us to explain the role of Ne for enhancement of H^- production by evaluation of the contribution of the elementary processes concerning H^- production. These estimations show that in both H_2 and (H_2+Ne) hollow cathode discharges the main

Table 4. Calculated Values of H^-, $H_2{}^+$, H^+, H, and Ne^+ Concentrations

	Concentration (cm^{-3})	
	H_2 Discharge	($H_2 + 90\%$Ne) Discharge
H^-	0.8×10^7	3.2×10^8
$H_2{}^+$	4.0×10^{10}	3.8×10^9
H^+	7.9×10^7	8.1×10^6
H	1.3×10^{13}	3.1×10^{12}
Ne^+	–	1.7×10^{11}

elementary process for H^- arising is the dissociative attachment of electrons to H_2. The contribution of electron attachment to H is smaller than 1%. The process of dissociative attachment is ~ 5 times more effective in the mixture than in pure H_2 discharge. This is caused by the increase of n_e giving rise to increased population of $H_2(v)$ states. We can also note that when **v** increases the H_2 (v) population decrease is faster for pure H_2 than for ($H_2 + 90\%$Ne) mixture, i.e., the $H_2(\mathbf{v} = 5)$ state population is only 20% lower for pure H_2 discharge than for the mixture, while the $H_2(\mathbf{v} = 9)$ population decreases by one order of magnitude in the above mentioned cases. Our calculations show that the collisions of H^- with H_2 are the most important for H^- destruction in both discharges and they are only slightly influenced in the mixture. The contribution of the collisions of H^- with H and with Ne^+ is much lower for H^- destruction. Finally, it is clear that the increased by one order of magnitude H^- concentration is caused by more effective H^- arising in ($H_2 + 90\%$Ne) mixture than in pure H_2 hollow cathode discharge.

We can conclude that the mixture of H_2 and Ne provides more appropriate conditions for enhanced H^- production. This result is important for the applications of the hollow cathode discharge as a source of hydrogen negative ions, for example in the technologies for new material development, in mass-spectrometry, in plasma fusion and etc.

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