Equilibrium density of h- in a low pressure hydrogen plasma
E. Nicolopoulou, M. Bacal, H.J. Doucet

To cite this version:

HAL Id: jpa-00208710
https://hal.archives-ouvertes.fr/jpa-00208710
Submitted on 1 Jan 1977

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
EQUILIBRIUM DENSITY OF H⁻ IN A LOW PRESSURE HYDROGEN PLASMA

E. NICOLOPOLLOU (*), M. BACAL and H. J. DOUCET
Laboratoire de Physique des Milieux Ionisés (**), Ecole Polytechnique, 91128 Palaiseau Cedex, France

(Reçu le 22 mars 1977, accepté le 19 juillet 1977)

Abstract. — The equilibrium density of hydrogen negative ions in a hydrogen low pressure plasma was calculated taking into account the various known production and destruction processes. It is shown that in most plasma conditions the contribution of dissociative recombination to H⁻ production is essential. Due to this process higher H⁻ densities are calculated than those obtained when dissociative electron attachment only is considered. However the calculated densities are ~ 100 times lower than the experimental values found in low pressure hydrogen plasmas. This discrepancy suggests that the dominant negative ion formation process in hydrogen plasma has not yet been identified.

1. Introduction. — Until recently it has been generally considered that the main processes leading to H⁻ formation in hydrogen plasmas are the electron collision processes with neutral molecules in the ground state, such as dissociative electron attachment [1, 2]:

\[ e + H_2 \rightarrow H^- + H \quad (1a) \]

and polar dissociation [3] which can be considered as a form of dissociative attachment:

\[ e + H_2 \rightarrow H^+ + H^- + e \quad (1b) \]

and becomes energetically possible above the electron energy of 17.2 eV.

However, the calculation of the density of H⁻ ions in a hydrogen plasma by considering the equilibrium between the formation and destruction rates for these ions led to the conclusion that dissociative electron attachment and polar dissociation reactions could not explain the high current densities observed in various negative ion sources [4, 5]. Demirkhanov et al. [6] suggested that formation of H⁻ ions by dissociative recombination:

\[ e + H_2^+ \rightarrow H^- + H^+ \quad (2a) \]
\[ e + H_3^+ \rightarrow H^- + H_2^+ \quad (2b) \]

could be essential in a plasma. The cross-section for reaction (2a) has been calculated theoretically by Dubrovsky et al. [7]; the threshold for this reaction is around 2 eV and the cross-section stays at about $10^{-17}$ cm² up to 4 eV. Only recently the experiments of Peart and Dolder [8] confirmed the existence of reaction (2a). We expected that taking into account this new process of H⁻ production in calculating the H⁻ density, would essentially improve the agreement between calculated equilibrium negative ion density for a hydrogen plasma and the measured one.

2. The continuity equation. — The continuity equation for H⁻ ions should include terms describing their production, destruction and diffusion. In the steady-state it will have the form:

\[ k_1 n_0 n_e + k_2 n_e n_e - k_3 n_e n_- - k_4 n_e n_- - \frac{n_-}{\tau} = 0 \quad (3) \]
The first term describes the production of $H^-$ by
dissociative electron attachment (including polar
dissociation) ($n_0$ — density of $H_2$ molecules, $n_e$ —
electron density), the second term, the production
of $H^-$ by dissociative recombination ($n_+^-$ density
of positive ions; thus it is assumed that most positive
ions are molecular; this assumption is supported by
the mass analysis of the positive ion species present
in a low pressure diffusion type hydrogen plasma [5]).
The third and fourth terms describe the destruction
by collisional electron detachment and mutual neu-
tralization, respectively ($n_-$ density of negative
ions); the last term represents the diffusion loss
($r$ is the diffusion loss time). $k_1$ — $k_4$ are the reaction
rates for the corresponding processes. Assuming that
the electron energy distribution is maxwellian, the
reaction rates for the electron collision processes
($k_1$ — $k_3$) have been calculated for various electron
temperatures, using established values for the cross-
sections. The variation of these rates with the electron
temperature is represented on figure 1. The cross-
section values used in calculating the reaction rates [9]
are taken from references [1] and [2] for the dissociative
electron attachment ($^1$), from reference [7] for $H^-$
formation by dissociative recombination and from
references [11] and [12] for the collisional electron
detachment. For the mutual neutralization rate involving
an atomic negative ion and a molecular positive
ion ($H^- + H_2^+ \rightarrow$ neutrals) very little is known except
for an estimate of the low energy rate of about
$10^{-7}$ cm$^3$/s [13]; this value of $k_4$ is used in our calcu-
lation.

Substituting into eq. (3) the expression for the
electron density which results from plasma neutrality :

$$n_+ = n_e + n_-$$

an equation of second degree for $n_-$ is found; the
solution of this equation for a given neutral density
and electron temperature gives the $n_-$ value as a
function of plasma density.

The electron temperature enters only indirectly
in the continuity eq. (3); however its influence on $n_-
$ is essential due to the strong dependence of the reaction
rates $k_1$, $k_2$ and $k_3$ on electron temperature
(Fig. 1). This conclusion is supported by figure 2,
which presents the calculated variation of the negative
ion density versus plasma density, for a hydrogen
pressure of $10^{-3}$ torr; here the parameter is the elec-
tron temperature. In this calculation the diffusion
loss of negative ions is neglected. It is obvious that

the $H^-$ production by dissociative recombination
becomes comparable to the $H^-$ production by disso-
ciative electron attachment, when the degree of gas
ionization is high enough :

$$\frac{n_+}{n_0} \geq \frac{k_1}{k_2}.$$  

In most plasma conditions the recently discovered
dissociative recombinaison (reaction 2) produces
more $H^-$ ions than the usual dissociative electron
attachment (reaction 1). The $H^-$ densities calculated
by our model, which takes into account reaction 2a,
are much higher than those predicted when reaction 2a
was neglected. However, these densities are still
about 100 times lower than the experimental values,
which we observed in various types of low pressure
hydrogen plasma. This discrepancy persists when we
take into account in the calculation other $H^-$
production processes, such as radiative electron
attachment to hydrogen atoms [14], dissociative elec-
tron attachment to $H_2O$ molecules [14, 15], surface
ionization of $H_2$ molecules [16]. The first two processes
are related to the presence in the plasma of impurity
species such as $H$ atoms and $H_2O$ molecules, while

($^1$) Few experimental data are available for the cross-section of
polar dissociation; this cross section rises with electron energy
but only the relative yield of $H^-$ has been measured in the range
of electron energies from 20 eV to 40 eV [3]. Following some other
authors [4, 10] we have extrapolated the cross-section values assum-
ing a rise up to 200 eV. This assumption needs to be justified by
further measurements; however the contribution of polar disso-
ciation is negligible when the electron temperature is lower than 5 eV.
the last one is due to the presence in the plasma of a hot electron emitting surface.

This discrepancy also persists when the effect of a beam of fast electrons (60 eV) which is injected in the gas to provide its ionization is taken into account. Let us note by $F$ the ratio between the density $n_{ef}$ of the fast monokinetic electrons, and the density $n_e$ of the maxwellian electron population. Thus:

$$F = \frac{n_{ef}}{n_e}$$

(6)

and

$$n_+ = n_e + n_{ef} + n_-.$$  

(7)

The solution of the continuity equation, which takes into account both a maxwellian electron population and a beam of monokinetic electrons [9], gives the dependence of the negative ion density on plasma density, for a given value $F$. The results are plotted in figure 3, with $F$ as a parameter. It may be noted that for a beam of 60 eV, the effect of the fast electrons on the negative ion density is negligible when $F \leq 10^{-2}$.

In a plasma produced by the injection of a fast electron beam, the higher limit for $n_{ef}$ can be estimated from the following:

$$n_{ef} \leq \frac{I_d}{eS} \left( \frac{2eV_d}{m_e} \right)^{-1/2}$$

(8)

where $I_d$ and $V_d$ are, respectively, the current and voltage of the discharge produced between the hot filament and the anode of the electron gun, and $S$ is the surface of the plasma section. Using eq. (8), we found that in our experiment:

$$F \leq 1.7 \times 10^{-3}.$$

According to figure 3, for these low values of $F$ the effect of a fast electron beam can be neglected in calculating the negative ion density. For this reason we did not consider the fast electron beam in eq. (3).

3. Experimental. — Limpaecher and MacKenzie [17] first used magnetic walls to produce a large, homogeneous plasma, which they denoted as a multipole plasma. The magnetic field, created at the plasma surface by a great number of small permanent magnets, reflects the plasma electrons and ions. Thus, with a given source of ionizing electrons, a higher degree of gas ionization is attained.

We have shown [9] that, unlike the electrons and the positive ions, the negative ions are not confined in the multipole plasma. We found, however, that a hybrid multipole plasma contains very high negative ion densities, but does preserve the profitable pro-
perty of the multipole plasma, namely the lower gas density required for its operation. The hybrid multipole plasma is characterized by the presence, besides the magnetic walls, of non-magnetic electrodes, collecting a non-negligible electron current.

It has been demonstrated by Taillet [18] that the presence of negative ions in high-frequency plasmoids leads to a flat potential well profile with sharp boundaries. The systematic exploration of various other types of plasmas produced in electronegative gases showed that they were highly homogeneous with respect to plasma potential and the charged particle densities over large plasma volumes. The magnetic multipolar confinement further improves this homogeneity.

The experimental results presented here were found in a hybrid multipole plasma. This plasma is produced in a cylindrical multipole magnetic structure, which we denote as a magnetic cage, since it consists of a great number of metal rods, containing small permanent magnets. The disposal of these magnets, illustrated on the insert to figure 4, is such that they form a succession of magnetic mirrors, surrounding the plasma. At one of the ends of the multipole cage, the multipole magnetic field is replaced by a non-magnetic grid. The gas is ionized by the electrons emitted by a tungsten filament, biased negatively (by 60 V) with respect to the multipole cage and the non-magnetic grid, which are at the same potential.

The apparatus used is a bi-plasma multipole device, shown in figure 4. A 50 l glass vessel contains two multipole cages, separated by a non-magnetic grid. Each multipole cage contains a tungsten filament; in the experiments described here only one of the filaments was heated; the negative and positive ion densities reported are relative to the cage in which the filament was heated. These densities were measured with a thin cylindrical electrostatic probe; the method used for determining the negative ion density with the mentioned electrostatic probe was described by Doucet [19].

4. Results and discussion. — The plasma density is varied at constant hydrogen pressure (10⁻³ torr) by varying the electron emission of the tungsten filament. The measured negative ion density is plotted versus the positive ion (or plasma) density on figure 5. It is found that the negative ion density continuously increases with plasma density and attains very high values (~ 3 × 10⁹ cm⁻³).

The analysis of the exponential region of the probe characteristics (Fig. 6) shows that the electron energy distribution is non-maxwellian, but can be approximated by two maxwellian distributions, characterized by two different electron temperatures. The typical probe characteristic plotted on figure 6 shows that most of the plasma electrons refer to the population characterized by the lowest electron temperature; a small fraction only corresponds to the high electron temperature population. Figure 7 shows the variation of these two electron temperatures with plasma density. There is no evidence concerning the existence of any tail of the electron energy distribution, superior to the maxwellian.
It is interesting to compare the experimental results presented on figure 5 with the predictions of eq. (3). The solution of this equation is simplified when assuming a Maxwellian electron energy distribution and using the reaction rates plotted on figure 1 versus the electron temperature. Therefore we approximate in the calculation the actual electron energy distribution by a Maxwellian one, to which we attribute either the higher (curve A, fig. 5) or the lower (curve B, fig. 5) electron temperature, measured at the respective plasma density. According to figure 2, for plasma densities lower than $10^{10} \text{cm}^{-3}$, curve A corresponds to an overestimate, while curve B corresponds to an underestimate, of the negative ion density. Thus curves A and B in figure 5 represent respectively the higher and lower limits between which the negative ion densities corresponding to the actual electron energy distribution are situated.

In order to emphasize the fact that in figure 5 curve A, as well as curve B, were calculated using the experimentally determined electron temperatures, which varied with plasma density as shown on figure 7, we also plotted on Figure 5 two curves, C and D, calculated for two constant electron temperatures, 2.8 eV and 0.4 eV, which are the extreme electron temperatures corresponding to curve A.

Thus, the measured negative ion densities plotted on figure 5 are about 100 times higher than those calculated by solving eq. (3), which takes into account the main known $\text{H}^-$ production and destruction processes. As mentioned in paragraph 2 this discrepancy cannot be attributed to other known $\text{H}^-$ formation processes, which are neglected in eq. (3), or to the presence of a beam of fast electrons.

The shape of the $n_-$ vs $n_+$ dependence in figure 5 indicates that a non-linear $\text{H}^-$ formation process dominates. $\text{H}^-$ production by dissociative recombination (reaction 2) is such a non-linear process, and actually the shape of the experimental curve is similar to the calculated ones for the plasma densities when reaction 2 dominates; however, the measured negative ion densities are much higher than those predicted by eq. (3), which takes into account reaction 2a.

Let us assume that the reaction rate for $\text{H}^-$ formation by dissociative recombination of $\text{H}_2^+$ ($k_3$) used in our calculation is correct; then another non-linear $\text{H}^-$ formation process should be imagined to explain the observed dependence of negative ion density on plasma density; dissociative electron attachment to an excited hydrogen molecule is one of the possible non-linear $\text{H}^-$ formation processes. We assume that the density of the excited hydrogen molecules involved in this electron attachment process is proportional to plasma density.

The dissociative electron attachment to excited hydrogen molecules has not yet been observed experimentally. Abroyan et al. [20] suggested the possibility of $\text{H}^-$ formation in a plasma due to dissociative electron attachment to vibrationally excited hydrogen.
molecules. Two successive electron collisions are involved in this process:

\[
\begin{align*}
    & H_2^\text{--} + e \rightarrow H_2^{(v=n)} + e \\
    & H_2^{(v=n)} + e \rightarrow H^- + H.
\end{align*}
\]  

(6a) (6b)

Abroyan et al. [20] report that the cross section for \( H^- \) production due to these reactions has been calculated and found to be \( \sim 10^{-18} \text{cm}^2 \).

It is also possible to assume that the excited molecular species exhibiting dissociative electron attachment is the electronically excited metastable state of the hydrogen molecule \( c^3 \Pi_u \), which has a mean lifetime of 1 ms.

5. Conclusion. — The equilibrium negative ion density calculated for a hydrogen plasma using known formation and destruction processes is \( \sim 100 \) times lower than the density measured in a low pressure hydrogen plasma. This discrepancy shows that the known \( H^- \) formation processes are not sufficient to explain the actual density of \( H^- \) ions. The observed dependence of negative ion density on plasma density indicates that a non-linear \( H^- \) formation process dominates. Dissociative attachment to a hydrogen molecule in a \( c^3 \Pi_u \), electronically excited metastable state is suggested as a possible, although yet unknown, \( H^- \) formation process.

Acknowledgments. — This work was supported in part by Direction des Recherches et Moyens d’Essais. The authors acknowledge stimulating discussions with Professor Florence Fiquet-Fayard.

References

[9] Nicolopoulou, E., Production et confinement des ions néga-
tifs dans des décharges d'hydrogène à basse pression. Thèse 3e cycle Orsay (1976).
[20] Abroyan, M. A., Golubev, V. P., Komarov, V. L. and Tsue-