Hydrogen kinetics in expanding high density plasmas

HYDROGEN KINETICS IN EXPANDING HIGH DENSITY PLASMAS

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ABSTRACT

With a 10 kW DC cascaded arc plasma source a production of up to 5×10^{21} H^{o}/s is achieved in full hydrogen, the dissociation degree being above 70%. After expansion into a low pressure background, the dissociation degree, measured by active actinometry and Rayleigh depolarization scattering, drops drastically. It appears that wall association leads to molecular hydrogen which re-enters in the expanding plasma beam. Using a simplified model, it is reasoned that diluting hydrogen with argon should not necessarily lead to a proportional loss in atomic hydrogen concentration.

INTRODUCTION

Since hydrogen atoms have a high chemical reactivity and penetration ability, they are widely used in both homogeneous and heterogeneous processes. As an example of the former, one could think of the chemical modification of light organic compounds (radicalization or polymerization). Concerning heterogeneous processes, the etching power of atomic hydrogen is used to regulate plasma deposition in order to obtain high quality material. Hydrogen atoms are also used for passivation of dangling bonds in amorphous hydrogenated silicon, a material used in photovoltaic cells, or for the reduction of oxides and the removal of chloride infections from iron archaeological artefacts for purpose of conservation. From atomic hydrogen, H^{-} can be produced by surface conversion at a cesium surface. These ions can be accelerated and neutralized in order to heat a fusion plasma by means of neutral beam injection. All these examples make clear that there is great demand for a high intensity source of atomic hydrogen.

EXPERIMENTAL

The plasma source we use is a wall-stabilized cascaded arc operated at subatmospheric pressure (0.6 ± 0.2 bar), with three cathodes at the upstream side, a stack of electrically floating copper cascade plates and a rocket-shaped anode nozzle. The latter serves as the connection to a heavily pumped cylindrical vessel having a length of 40cm and 40cm diameter (Fig. 1). As the pressure in this vessel is around 100 Pa, a supersonically expanding plasma jet is obtained.

The pressure and voltage drop at each plate can be monitored, as well as the heat transfer from the plasma to the plate wall. The latter is derived from the temperature rise of the cooling water passing through that particular plate (temperature is measured with semiconductor thermosensors and water flow with rotation type flow transmitters). As also the input power is known from the voltage drops and the arc current, the power transferred to the plasma can be calculated, as well as the general energy efficiency. Plasma power is dissipated in heating, dissociation and ionization. The dissociation degree, defined as [H]/([H]+2[H$_2$]),can therefore be determined in the arc, provided the ionization degree and the temperatures of ions, electrons, atoms and molecules at the arc exit are known.
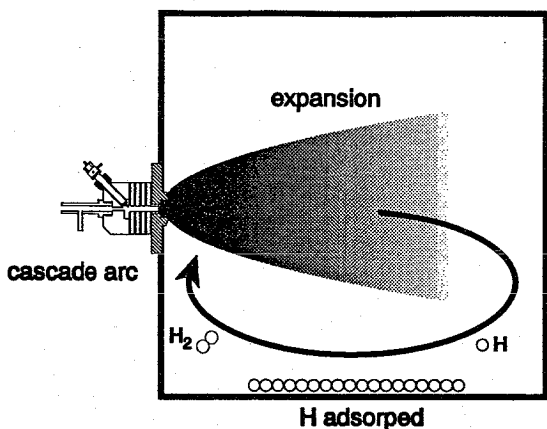
expansion

cascade arc

H_2

O H

H adsorped

ACTIVE ACTINOMETRY

The local dissociation degree in the expansion has been measured with RF excited active actinometry. *Active* actinometry is needed since electronic excitation is absent due to the low electron temperature: between 0.15 and 0.4 eV (excited states are populated only by recombination reactions; passive line-emission spectroscopy can therefore only be used to monitor recombination reactions). In active actinometry, the electrons are locally heated by an RF probe exciter with typical powers of 10 W. As a result H Balmer lines and the H_2 Fulcher rovibrational band are excited and can be spectroscopically observed. In the case of dominant direct excitation from the ground state by electrons, the intensity of the Balmer H_α line (atomic transition from n=3 to n=2) depends on the ground state density of the atoms $n_{0,at}$, the amplitude of the electronic excitation cross section from n=1 to n=3 $\sigma_{1,3}$, the radiative transition probability from n=3 to n=2 $A_{3,2}$, the radiative lifetime of the n=3 state τ_3, and an energy-dependent term, including the form function of the atomic excitation cross section $\phi_{at}(\epsilon)$, the electron energy distribution function $f(\epsilon)$ and the threshold energy for excitation from n=1 to n=3 (12.09 eV):

$$I_{at} = n_{0,at}\sigma_{1,3}A_{3,2}\tau_3 \int\limits_{12.09eV}^{\infty} \phi_{at}(\epsilon)f(\epsilon)\sqrt{2\epsilon/m_e}d\epsilon.$$

Accordingly, the intensity of the Fulcher $3p^3\Pi_u(v'=0, J') \to 2s^3\Sigma_g(v''=0, J''=J')$ Q lines depend on the ground state density of the molecules $n_{0,mol}$, the amplitude of the emission cross section σ_{em}^{0-0} (including electronic excitation from $X^1\Sigma_g^+$ (v=0) to $3p^3\Pi_u$ (v=0), but *also* radiative deexcitation to $2s^3\Sigma_g$ (v=0); it is summed over *all* J) where we have used that in the ground state v=0 in our plasma, and a similar energy-dependent term:

$$\sum_J I_{Q(J)} = n_{0,mol}\sigma_{em}^{0-0} \int\limits_{13.97eV}^{\infty} \phi_{mol}(\epsilon)f(\epsilon)\sqrt{2\epsilon/m_e}d\epsilon.$$

If we assume the form functions ϕ_{at} and ϕ_{mol} to be similar, an approximative expression for the ratio $n_{0,at}/n_{0,mol}$ can be derived:

$$\frac{n_{0,at}}{n_{0,mol}} \approx \frac{[H]}{[H_2]} = \zeta \frac{I_{at}}{\sum_J I_{Q(J)}} \frac{\sigma_{em}^{0-0}}{\sigma_{0,3}A_{3,2}\tau_3}$$

where ζ is a correction factor for the difference in threshold of the atomic and molecular excitation processes. Assuming a Maxwellian velocity distribution $f(\epsilon)$ with an electron temperature in the

range 2.5 - 4.5 eV (typical values for RF-probe excited plasma) and step-like form functions, this factor is calculated to be 0.6±0.1. The radiative excitation cross section σ_{em}^{0-0} has been calculated by /1/, the atomic excitation cross section $\sigma_{1,3}$ is calculated by /2/ and the Einstein transition probability $A_{3,2}$ and the radiative lifetime τ_3 can be found in /3/.

RAYLEIGH DEPOLARIZATION SCATTERING

Rayleigh depolarization scattering is based on the phenomenon that, when making use of polarized incident radiation, the 90° Rayleigh scattered radiation is fully polarized only if the scattering objects are spherically symmetric, e.g. in the case of ground-state atoms /4/. In the case of non-spherically symmetric molecules a small component of the scattered radiation is depolarized. The ratio of the depolarized (say, horizontal) and polarized (vertical) scattering components I_h/I_v for the linear hydrogen molecule is, for 532 nm radiation and a temperature of 300 K: $\rho_{Rayl,H_2} = 2.3 \times 10^{-3}$ /5/. This ratio slightly depends on the rovibrational state of the scattering molecules, and it therefore changes about 10% for a gas temperature change from 300 to 1400 K. Since the depolarization effect is very weak, the lower detection limit is estimated to be around 10^{21} H_2 molecules per m³ in our experiment. A description of the complete Thomson-Rayleigh setup can be found elsewhere /5/.

RESULTS

DISSOCIATION DEGREE IN THE ARC

In pure hydrogen, the general energy efficiency was found to be 35±5%, independent of the input flow, ranging from 4 to 9 SLM (when using less than 10% hydrogen in argon, the general efficiency is higher, increasing to 48% in pure argon). For purpose of calculating the dissociation degree, the ionization degree is estimated to be less than 2.5% in full hydrogen (increasing to 10% in pure argon), and the temperature of atoms, ions and electrons 1 eV. Surviving molecules, if any, come from the periphery of the arc where the electron temperature is lower: the molecular temperature is estimated to be less than 0.4 eV. From the input power, a lower limit for the dissociation degree is calculated and plotted as a function of hydrogen gas input flow in Fig. 2. The atomic hydrogen flow derived from this is shown in Fig. 3.: a production of up to 5×10^{21} H°/s is achieved with 10 kW input power.

ACTIVE ACTINOMETRY

From the ratio of the mentioned atomic and molecular line intensities, density ratios are determined. Fig. 2 (bottom curve) shows the resulting dissociation degree at $z=250$ mm from the arc exit as a function of input flow. The background pressure was 130 Pa and the arc current was 37 A; the RF probe exciter power was 20 W. Not only has the dissociation degree dropped to a much lower value than in the source (10% instead of more than 70% in the arc), but it also increases with the gas flow, whereas in the source, the opposite is observed.

RAYLEIGH DEPOLARIZATION SCATTERING

The measured depolarization ratio was $\rho_{Rayl,H_2} = (2.2 \pm 0.3) \times 10^{-3}$, in good agreement with the theoretical value. In the hydrogen plasma ($I_{arc}=37$ A, $P=8$ kW, H_2 flow=3.0 SLM, $p=715$ Pa), the local (detection volume ≈ 0.25 mm³) depolarization signal at $z=15$ mm from the expansion nozzle was 160±50 counts for 1800 s measuring time. The hydrogen molecular density was calculated to be $(3\pm1)\times10^{22}$ m⁻³. This value gives with the estimated temperature a pressure contribution of more than 75% of the measured pressure. Hence also this measurement (performed in another apparatus) confirms the dominance of H_2 molecules rather than the H atoms of the source.
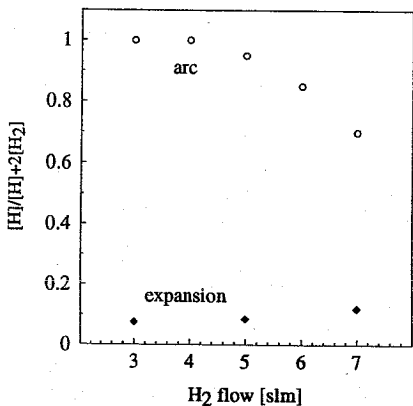
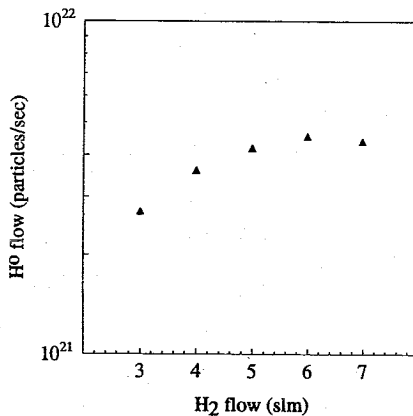Fig. 2. *The dissociation degree in the arc and in the expansion.*

Fig. 3. *The atomic hydrogen flow out of the arc plasma source, derived from fig. 2.*

DISCUSSION

The observation that the dissociation degree drops in the expansion leads to the hypothesis that in the reactor the highly dissociated plasma is strongly mixed with the cold background gas. Since the molecular hydrogen flow from the arc is low, hydrogen molecules must be created in the expansion vessel. Wall association

$$H + H(adsorped) \overset{wall}{\rightarrow} H_2(desorped)$$
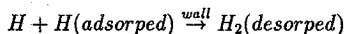
is known to be effective and to result in hydrogen molecules[1]/6/. Together with a strong recirculation flow, this wall association process will provide a reentry flow of hydrogen molecules into the plasma jet.

In order to understand the observed *increase* in dissociation degree in the vessel with increasing flow, we consider the following crude model. First of all, assume the ratio of atoms and molecules to be proportional with the ratio of the circulation time and residence time:

$$\frac{[H]}{[H_2]} \sim \frac{\tau_{circ}}{\tau_{res}}$$

based on the assumption that the atom, when in the recirculation flow, adsorbs to the wall and associates to form a molecule. The average lifetime of an atom is thus proportional to the time required to complete one circulation. This time is given by:

$$\tau_{circ} \approx \frac{L}{v_{rec}} \approx \frac{A}{A_{jet}} \frac{T_{jet}}{T_{rec}} \frac{L}{v_{jet}}$$

where L and A are the vessel length and cross section area respectively, v_{jet}, A_{jet} and T_{jet} are the jet flow velocity, cross section area and gas temperature, and v_{rec} and T_{rec} are the velocity and gas

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[1]Although it is argued that a significant fraction of the desorped molecules are rovibrationally excited /6/, the characteristic vibrational quenching time to v=0 is, based on rate coefficients from /7/, estimated to be in the order of 1 msec, whereas the residence time in the vessel is typically 0.5 sec. A vast majority of the molecules will therefore be in the v=0 state. The presence of a small fraction of vibrationally excited molecules is confirmed by the observation of anomalous fast loss of ionization in the expansion, due to a sequence of charge exchange $H^+ + H_2^{\nu \geq 4} \rightarrow H_2^+ + H$ and dissociative recombination $H_2^+ + e \rightarrow H + H$ /8/

temperature of the recirculation flow. The equation is based on the consideration that the jet flow and the recirculation flow must be balanced: $n_{jet}v_{jet}A_{jet} = n_{rec}v_{rec}A_{rec}$. If we assume the pressure in the jet and the recirculation to be equal, this leads to $v_{jet}A_{jet}/T_{jet} = v_{rec}A_{rec}/T_{rec}$. Finally, we have used that $A_{jet} \ll A_{rec} \approx A$ and thus $v_{jet} \gg v_{rec}$. A typical value for the recirculation time is 5 msec.

The residence time (in our setup typically 0.5 sec) is the time a particle resides in the vessel before being pumped away, and it is given by

$$\tau_{res} = \frac{nV}{\Phi} = \frac{pV}{kT_{rec}\Phi}$$

where n is the average particle density, Φ is the pumping speed in particles per second (which is, during stable operation, equal to the incoming particle flow), p and V are vessel pressure and volume respectively, and k is the Boltzmann constant. Considering that the loss process for atoms is wall association and the loss process for molecules is being pumped out, we thus find:

$$\frac{[H]}{[H_2]} = \frac{\kappa}{v_{jet}} \frac{\Phi}{p}$$

κ being a proportionality constant (containing a.o. the dissociation degree from the arc, jet gas temperature and the cross section area of the plasma jet). When increasing the input flow at constant vessel pressure (this means that the pumping speed Φ must be increased), our crude model predicts an *increase* of the dissociation degree, as has been observed in the experiments. Note that operation at low pressure also gives a high dissociation degree, provided the cross section area of the jet does not increase too much.

Since the mass of an argon atom is 40 times that of a hydrogen atom, its acoustic velocity is lower by a factor six. As a lower velocity leads to a longer circulation time and thus to a higher ratio $[H]/[H_2]$, we will extend our crude model to also encompass argon/hydrogen mixtures.

First, we define α as being the atomic hydrogen fraction leaving the source: $\alpha = [H]/([H]+[Ar])$, and μ as being the molecular hydrogen fraction in the input gas: $\mu = [H_2]/([H_2]+[Ar])$. We impose that the total particle input be constant: $[H]+[Ar]\equiv 1$ (this implies that the total *input* flow decreases for increasing hydrogen fraction). Furthermore, we assume that all flow velocities scale with the acoustic velocity, giving an effective jet velocity $v_{jet} = \alpha \cdot 6v_{Ar} + (1 - \alpha) \cdot v_{Ar} = (1 + 5\alpha) \cdot v_{Ar}$. The atomic hydrogen density increases with α (representing more hydrogen input), but decreases with v_{jet}:

$$[H] \sim \frac{\alpha}{1 + 5\alpha} = \frac{2\mu}{1 + 11\mu}$$

where we assumed full dissociation in the arc, giving $\alpha = 2\mu/(1+\mu)$. The result is shown in Fig. 4, where the atomic hydrogen density is normalized to the full hydrogen case ($\mu=1$). Note that as a boundary condition we have imposed constant particle input: if $\mu=0$ corresponds to x SLM argon gas, $\mu=1$ corresponds to $x/2$ SLM hydrogen gas.

From Fig. 4 it can be seen that, according to our crude model, the atomic hydrogen density does not decrease dramatically when diluting hydrogen with argon. In fact, using 4% hydrogen and 96% argon (explosion limit) results in an atomic hydrogen density which is still 33% of the full hydrogen case. Here, hydrogen enrichment due to the higher pumping speed for argon when compared to hydrogen, has even been neglected. The use of small hydrogen fractions offers some other features: ionization is maintained longer /8/, arc operation is more simple and more safe and there is more efficient energy conversion to the plasma. The latter is of specific importance for applications where there is a large heat flux required, e.g. plasma treatment of iron archaeological artefacts /9/.
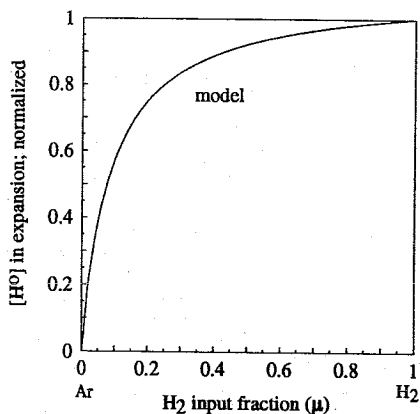
Fig. 4. The atomic hydrogen density as a function of the hydrogen fraction in the input gas, normalized with respect to the full hydrogen case, according to the crude model. We have imposed the input flow of argon + hydrogen atoms to be constant; x slm argon at $\mu=0$ therefore corresponds to x/2 slm H_2 at $\mu=1$.

CONCLUSIONS

With a 10 kW DC cascaded arc up to 5×10^{21} H°/s can be achieved. In the expansion, dissociation is lost due to the presence of recirculating hydrogen molecules, produced by wall association of hydrogen atoms. The highest dissociation degree is obtained using low pressure and high pumping speed. The use of argon/hydrogen mixtures does not imply a proportional loss of atomic hydrogen density, whereas it offers some practical benefits.

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