A NEW METHOD FOR QUANTIFICATION OF HYDROGEN ABSORBED AT THE CATHODE OF A GLOW DISCHARGE USING OPTICAL SPECTROSCOPY*

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In this paper, a new method for obtaining a qualitative measure of the amount of hydrogen stored at the cathode of a glow discharge is presented. The method is based on the M effect and consists on observing spectral changes of the discharge on addition of hydrogen desorbed by the heated cathode. For this purpose, hydrogen was introduced in the cathode volume using plasma of pure hydrogen. The working gas was neon and the electrodes were made of Ti.

The M effect consists on the emission of a nearly monochrome spectrum of a discharge in electronegative-electropositive gas mixtures at relatively elevated pressures. Here, the electronegative gas was hydrogen and the electropositive gas was neon. As the intensity of the M effect depends directly on the amount of hydrogen present in the discharge, a direct measure of the relative quantity of hydrogen released by the cathode can be obtained.

Key words: hydrogen storage, luminescent discharge, M-effect, ion-ion recombination.

1. INTRODUCTION

A few decades ago, a large amount of work was dedicated to the study of elementary processes in ionized multiple gas mixtures at elevated pressures, one of the objectives being to obtain Penning type lasers. In such lasers, lower excited states are quenched faster than upper excited levels due to inelastic heavy particle collisions [1–4]. Schmieder *et al.* [5–6] have reported generation of the first almost continuous laser radiation using a dielectric barrier discharge at elevated pressures in Ne-H_2 at 585.3 nm. Full explanation of the appearance of this line has not been given yet. In previous work aimed at studying dielectric barrier discharges, a new effect that is believed to be at the origins of this laser radiation was reported by our group [7–13]. The effect consists on the selective emission of a

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single spectral line under certain plasma conditions. This was called the Mono-chromatisation effect (the M effect). This effect may be useful for explaining processes in known lasers and may also be important for developing new lasers, new monochromatic light sources, sources for standard reference spectral lines, etc.

A brief description of the M-effect will be presented in the following.

2. THE MONOCHROMATISATION EFFECT (M-EFFECT)

The M-effect consists of a drastic change of the optical emission spectrum of neon on addition of hydrogen [7–11]. Practically, for certain values of the working parameters, the emission spectrum of neon was reduced to a nearly monochrome radiation having $\lambda = 585.3$ nm.

The main working parameters of the discharge for which the M-effect has been previously put in evidence in a d.c. are: 5–60 mA/cm^2 current density, 15–90 torr total gas pressure, 10%–50% hydrogen percentage in the Ne + H_2 mixture [9].

As we have previously shown [12], the M-effect is due to an ion-ion recombination process. The main reaction that is believed to take place is the energy resonant three body reaction:

$$\mathrm{Ne}^{+} + \mathrm{H}^{-} + \mathrm{H}_{met}(n=2) \;\rightarrow\; \mathrm{Ne}^{*}(2p_1) + \mathrm{H}^{*}(n=3) + \mathrm{H} \qquad (1)$$

followed by a radioactive dezexcitation

$$\mathrm{Ne}^{*}(2p_1) \rightarrow \mathrm{Ne}^{*}(1s_2) + hc/\lambda_1 \qquad \lambda_1 = 585.3 \text{ nm}$$

where λ_1 corresponds to the radiation resulted from the M-effect. The M parameter is a measure of the intensity of this effect and was defined as the ratio of the intensities of two neon lines at λ_1 = 585.3 nm and λ_2 = 614.3 nm, as written in eq. (2).

$$M = \frac{I_{585.3nm}}{I_{614.3nm}} \qquad (2)$$

The value of M in the case of pure Ne plasma lies within a few units whereas on addition of hydrogen, a value as high as 20 was obtained.

The M-effect appears in electropositive-electronegative gas mixtures only. Another condition is that the plasma parameters are chosen so that negative ion generation by electron attachment to hydrogen is ensured [12].

This effect was also observed in narrow gap a.c. barrier discharges [8], where the M parameter as high as 40.

3. EXPERIMENTAL ARRANGEMENT

The experimental device consisted of a cylindrical glass tube of 28 mm diameter having two identical titanium electrodes of 8 mm diameter, 6 mm length, and 10 mm distance between the electrodes. Ti was used as cathode material due to its property to absorb and desorb hydrogen easily when heated.

The discharge tube was connected to a high vacuum pumping unit and also to a glass made gas-filling system. The electrodes were powered using a d.c. high voltage supply.

The optical emission spectra of the plasma was obtained using a standard mounting consisting of a VARIAN TECHTRON spectrometer, an EMI type PhM and a recorder.

The experiment was focused on determining the value of the M parameter for the plasma ignited in pure neon, with and without hydrogen stored in the cathode volume. The main steps of the experiment were:

Step 1

- pump down to10^{-5} torr;
- pure neon was introduced at 8 torr;
- ignition and maintenance of a d.c. discharge current of 7.5 mA for 25 minutes;
- measurement of line intensities of the two wavelengths of interest and calculation of the *M* parameter according to relation (2). The measurements were taken every 1 minute for a duration of 25 minutes.

The power supply was then turned off and the chamber pumped down to 10^{-5} torr. This experiment provided a reference value of the *M* parameter, when the plasma contained only pure neon.

Step 2

- pure hydrogen was then introduced at a pressure of 16 torr;
- a discharge in pure hydrogen was ignited. A 40–50 mA current was applied for 20 minutes. The cathode temperature was around 700°C;
- the power supply was then turned off and the cathode was left to cool down in hydrogen atmosphere for 10 minutes;
- hydrogen was then pumped down to 10^{-5} torr.

This experiment was undertaken in order to introduce hydrogen in the volume of the Ti cathode.

Step 3

- pure neon was then introduced in the process chamber at a pressure of 10 torr. A 2 mA current was applied for 25 minutes;
- the optical spectrum was acquired every minute and the value of the *M* parameter was calculated for each measurement.

In this experiment, the desorption of hydrogen from the cathode during discharge ignition was put in evidence. Relative measurement of the amount of hydrogen present in the discharge was obtained.

4. RESULTS AND DISCUSSIONS

The value of the M parameter for the discharge in pure neon was around 2.5 a.u.

In Fig. 1, the time evolution of the *M* parameter for the experiment in pure neon described in Step 1 is shown. As can be seen in this figure, *M* varied slightly at the beginning and had a constant value thereafter. This behavior suggested that the discharge is stable only after a few minutes from ignition.

Fig. 2 shows the evolution in time of the *M* parameter before and after appearance of hydrogen in the discharge, as described at Step 2 and 3.

The presence of hydrogen is suggested by the jump to higher values of the *M* parameter. The low value of the *M* parameter observed after one minute from the ignition is probably due to the fact that discharge is unstable at the beginning. The smooth decrease of *M* observed is due to the continuous desorption of hydrogen stored in the titanium cathode.

The desorption rate depends on the temperature of the cathode during desorption and on the amount of hydrogen initially present in the cathode. In order

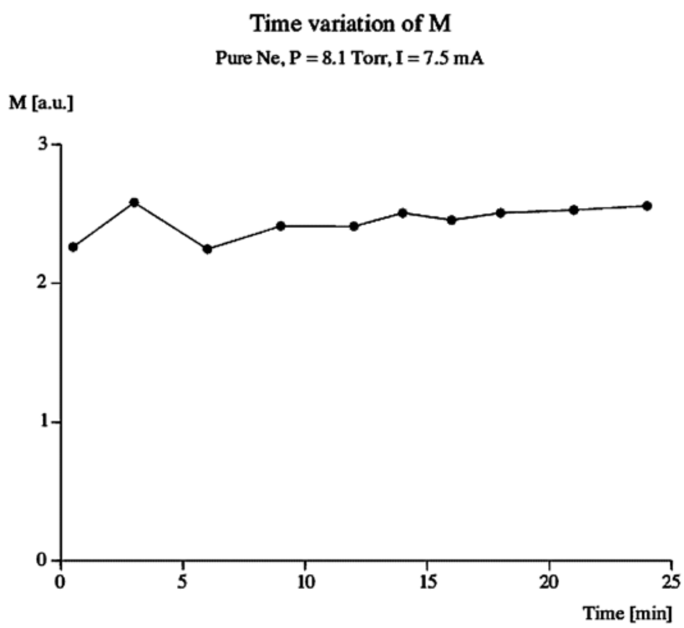

Fig. 1. – Time variation of the M parameter, discharge in pure Ne.

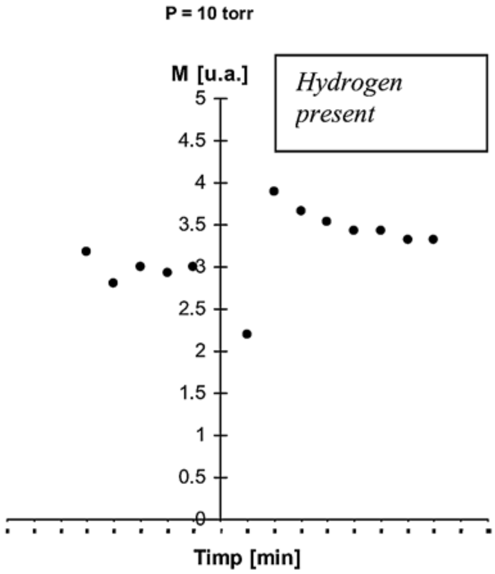

Fig. 2. – Temporal dependence of the M parameter. Left hand side: before introducing hydrogen; right hand side: after introducing hydrogen.

to put in evidence the desorption of hydrogen, a low value of the discharge current was used.

As the emission of the neon line at $\lambda_1 = 585.3$ nm is due an ion-ion recombination process (namely recombination of positive neon ions with hydrogen negative ions), the *M* parameter is proportional to the density of the hydrogen negative ions present in the discharge. Thus, a relative quantification of the amount of hydrogen present in the discharge can be easily obtained.

The *M* effect can be used for the titration of negative ions in plasmas.

5. CONCLUSIONS

The experimental data show the possibility to use the *M* effect in 10–100 torr glow discharges for monitoring the presence of hydrogen. Furthermore, this method can be used for evaluation of the density of the negative hydrogen ions in different plasmas.

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