THE ENERGY AND MASS DISTRIBUTION OF IONS AT THE CATHODE OF A D.C.
GLOW DISCHARGE IN METHANE/HYDROGEN MIXTURES

M. I. Lees
The Electricity Council Research Centre
Capenhurst, Chester, U.K.

ABSTRACT

The energy spectrum of ions at the cathode of a glow discharge in 5% CH4, 95% H2 at pressures of 1 to 6 torr and current densities of 2.4 to 24 Am^-2 have been measured. Hydrocarbon ions with energies of a few eV to an energy equivalent to the cathode fall voltage carry 75% of the ionic current. The results suggest that the ions CH3^+, CH2^+, CH^+, C^+ are produced by interactions between hydrogen ions and neutral methane molecules.

1. INTRODUCTION

The introduction of carbon into a steel surface is widely used for improving the wear and fatigue properties of industrial components. There is a significant increase in the carburising rate of a steel surface in a hydrocarbon atmosphere when it is made the cathode of a d.c. glow discharge. (1) Since the discharge does not affect the diffusion coefficient of carbon in the steel (2) the enhancement of the carburising rate is most probably due to mechanisms occurring in the cathode dark space and at the steel surface which cause the rate of transfer of carbon across the gas/solid interface to increase. To gain an understanding of the process the energy and state of species striking the surface must be known. In this paper an analysis of the mass and energy of positive ions which are incident on the cathode of a glow discharge in a hydrocarbon atmosphere is given.

2. APPARATUS

A schematic diagram of the apparatus is shown in Figure 1. The apparatus consists of a low vacuum chamber in which the discharge is struck and a high vacuum chamber in which the energy and mass analysers are mounted.

The discharge vessel is constructed from a 50mm I.D. glass cross and is pumped by a rotary pump. The gas feed and pumping lines occupy two opposite arms of the cross. Pressure is measured by a capacitance manometer mounted in the third arm. Gas composition and pressure are controlled to within 0.25% by a pressure/flow controller. The anode is a steel tube of length 20mm I.D. 40mm which is connected to the remaining arm. The cathode is a steel cup of 47mm I.D. with a raised base of 39mm O.D. It is connected to the anode by an alumina tube of 47mm O.D., 40.2mm I.D. and 100mm in length. This design ensures that conducting coatings on the alumina tube produced for example by sputter products or carbon are prevented from contacting the cathode thus preventing the area of the cathode from changing during an experiment. The base of the cup
is a 3mm thick replaceable steel disc. A 0.1mm radius hole is drilled at the centre of the disc and the region immediately surrounding the hole is 0.1mm thick.

Although the discharge chamber is operated at 1 to 10 torr the mean free path of ions in the energy and mass analysers must be greater than the distance travelled by the ions. To achieve this a separately pumped intermediate vacuum chamber between the discharge chamber and the analyser chamber is used (see Figure 1). This is made from stainless steel and is pumped by a 150mm oil diffusion pump. It operates at pressures between $10^{-3}$ and $10^{-4}$ torr. The distance from the cathode to the baffle between the intermediate vacuum chamber and the analyser chamber is 70mm. The analyser chamber is fabricated from stainless steel and is pumped by a 100mm oil diffusion pump giving a typical operating pressure of $2 \times 10^{-6}$ torr. The analyser and intermediate vacuum chambers are connected by a 3mm diameter aperture in the centre of the baffle.

Ions passing through the aperture in the baffle with a kinetic energy of zero at the centre element potential of a three element unipotential electrostatic lens are focussed onto the entrance aperture of a 90° spherical sector electrostatic energy analyser. The radii of the electrodes in the energy analyser are 110mm and 90mm and with a 2mm exit slit the analyser function is trapezoidal with a F.W.H.M. of 1% and a total bandwidth of 2% of the nominal pass energy. A three element electrostatic lens is used to decelerate the ions to energies of less than 30eV and focusses them at the entrance aperture of a quadrupole mass spectrometer.

To reach the electron multiplier and be measured, all ions which pass through the energy analyser must have a finite kinetic energy at earth potential. However the maximum energy of ions in the mass analyser must be of the order of 30eV. The energy analyser potentials are derived from a resistor chain and two power supplies so that ions whose locus is the centre line of the energy analyser have a kinetic energy $E$ in the mass analyser where:

$$E/2 < E < 30\text{eV} - E/2$$

and $E$ is the total bandwidth of the analyser.

To measure the energy spectrum of the ions at the cathode, the voltage of the cathode must be varied with respect to earth potential thus the discharge power supply is arranged to be floating.

3. EXPERIMENTAL METHOD

The energy dependence of the current of each of the ionic species incident on the cathode is measured by holding the pass energy of the analyser constant and varying the potential difference between the cathode and the analyser. This simplifies analysis of the data since under these conditions the resolution of the analyser is constant. In addition, the properties of the decelerating lens do not change with the energy of the ions being sampled and hence it does not affect the measured energy spectrum. Acceleration of the extracted ion beam also reduces the effects of space charge in the beam.

The results from hydrogen/methane mixtures were all measured with a constant pass energy of 1000eV at the energy analyser. A new mild steel cathode was used for each experiment. After replacement of the cathode the apparatus was left to pump for 48 hours. Prior to each experiment,
a preliminary treatment which consisted of a 30 minute exposure to a hydrogen glow discharge at 2 torr and 24 Am\(^{-2}\) was performed. During this treatment the discharge chamber was effectively outgassed allowing the base pressure in the discharge chamber to be reduced to less than 10\(^{-2}\) torr. At the end of this treatment it was possible, by observing the hydrogen ion energy spectrum to establish the correct functioning of the apparatus.

The energy spectra of the ions is built up from mass scans taken at a series of values of cathode voltage between the voltage at which the peak current of H\(_2^+\) is measured and the voltage at which no ion current is measured. The mass spectra are digitised and stored on floppy disc along with relevant experimental parameters for subsequent analysis.

Background removal, identification of peaks and measurement of the peak heights is performed by computer. A second difference minimum search is performed to identify the peaks.

The cathode fall voltage varies as changes are made in the discharge pressure, current or gas composition. For a meaningful comparison of spectra the results are expressed as a function of V/V\(_c\) where V is the energy of an ion divided by its charge and V\(_c\) is the cathode fall potential. V\(_c\) is deduced from the maximum energy of ions measured. The measured currents are normalised so the integral of current between V/V\(_c\) = 0 and V/V\(_c\) = 1 gives the total current of each ion.

4. RESULTS

Figure 2 shows the energy spectra of ions in a 100% H\(_2\) atmosphere at 2 torr and 24 Am\(^{-2}\). The results are similar to those in reference 3 for discharges in hydrogen. The logarithms of the measured current of H\(^+\), H\(_2^+\) and H\(_3^+\) are all approximately linearly dependent upon V/V\(_c\). H\(^+\) has the highest proportion of high energy ions and H\(_2^+\) has the lowest energy distribution. The ionic current is carried in the ratio I\(_{H^+}\): I\(_{H_2^+}\): I\(_{H_3^+}\) = 1:0.75:0.95.

When 5% methane is added to a hydrogen atmosphere the distribution of ionic current changes dramatically. There is a broad spectrum of ion energies at the cathode, ranging from a few eV to an energy equivalent to the full cathode fall voltage. The energy distribution of current of a particular ion depends upon the identity of the ion. Figure 3 shows the energy spectra of ions up to a mass to charge ratio of 16 A.M.U./e measured in a 5% CH\(_4\) 95% H\(_2\) atmosphere at 2 torr, 24 Am\(^{-2}\), 870V. Ions with a mass to charge ratio of up to 78 are seen in the mass spectra but are omitted for clarity. Ions containing one carbon carry 56% of the total measured ion current, with 16% carried by ions containing two carbons and 3% carried by ions containing 3 carbons. Only 23% of the ionic current is carried by hydrogen ions with the remaining current carried by higher hydrocarbons and impurity ions.

The energy spectra of the H\(^+\), H\(_2^+\) and H\(_3^+\) ions are similar to their energy spectra in a 100% hydrogen discharge. However there is a greater abundance of H\(_3^+\) than H\(^+\) throughout the spectrum and this is reflected in the relative total currents of the ions of I\(_{H^+}\): I\(_{H_2^+}\): I\(_{H_3^+}\) = 1:5.7:6.6. The introduction of 5% methane causes the H\(^+\) current to drop by a factor of 21, while the H\(_2^+\) and H\(_3^+\) ion currents only drop by a factor of 3.
The energy spectra of hydrocarbon fragment ions with a mass/charge ratio of 15(CH_3^+), 14(CH_2^+), 13(CH^+) and 12(C^+) display a systematic trend with increasing dissociation of the parent molecule. The value of V/V_C at which the maximum measured current is recorded, and the width of the distribution both increase in the series CH_3^+, CH_2^+, CH^+, C^+. The measured current at energies of a few eV decreases in the same series. Note that the current of C^+ is within a factor of 2 of the maximum over the range 0.25 < V/V_C < 0.8. A similar trend is displayed by ions with 2 and 3 carbons with the higher mass ions of each group tending to low energies and the lower mass ions displaying a similar distribution to C^+, although the energy range over which they are observed is reduced. C_2^+ is observed over the range 0.15 < V/V_C < 0.95 and C_3^+ over the range 0.3 < V/V_C < 0.9.

Energy spectra have been measured in discharges with a current density of 24Am^-2 for pressures between 1 torr and 6 torr and current densities between 2.4Am^-2 and 24Am^-2 at 2 torr. The energy spectra from discharges at constant pressure show a similar trend with decreasing current density to that observed for increasing pressure at constant current density. The proportion of current carried by H^+, H_2^+ and H_3^+ ions decreases and the proportion of current carried by hydrocarbon ions increases. There is a relative increase in the current of the H^+, H_2^+, H_3^+, CH_3^+ and CH_4^+ ions below V/V_C = 0.2 but no major change in the shape of the energy spectrum of other hydrocarbon ions. Hence the distribution of total ion current with V/V_C is approximately constant in the range 0.2 < V/V_C < 0.8 but a relative increase in the current below V/V_C = 0.2 is observed.

Figure 4 shows the variation of the proportion of current carried by each ion against the reduced current density J/n^2 where n is the number density of background gas molecules and it is assumed that the temperature of the gas in the cathode fall region is the same as the cathode temperature. the scatter of the data reflects the difficulty in obtaining an accurate integral of the current of each ion, particularly in the region of V/V_C < 0.1 where the spectra are modified by the extraction aperture and there is a large change in current across the energy range sampled by the energy analyser. However there is a definite correlation between the results measured at constant current and those measured at constant pressure.

5. DISCUSSION

The model suggested by Davies and Vanderslice(3) is of ion generation in the negative glow with resonant charge transfer collision in the dark space moderating the ionic energies. They found good agreement with experiment for ions of the parent gas. Ions having an appreciable collision cross section with the background gas have a distribution of current at the cathode which is approximately proportional to the inverse exponent of the ion energy. These observations are confirmed by this work. However, this model cannot explain the observed spectra of the hydrocarbon ions. For ions to be observed at an energy qV where q is the charge on the ion and where V is a significant fraction of V_C then the mean free path of the ions in the background gas must be large. Ions with a large mean free path which are created in the negative glow are predominantly observed at an energy qV_C. Since the observed current of hydrocarbon ions peaks at a fraction of V/V_C and the distribution of energies is large, then ions are created in the dark space.
The fraction of ions produced by electron ionisation of methane in the dark space is given by the ratio of the product of the ionisation cross section and number density for methane and hydrogen molecules. Taking a value of $10^{-20} \text{m}^2$ for the maximum cross section of hydrogen (4) and a value of $3 \times 10^{-20} \text{m}^2$ for methane (5) then the fraction of ions produced by the electron ionisation of methane is 0.15. This is much smaller than the measured fraction of 0.75. In addition the cracking pattern of methane from electron ionisation does not agree with the observed abundance of the hydrocarbon ions. Direct electron ionisation of methane in the dark space is therefore not the major mechanism for production of the hydrocarbon ions.

Interaction between energetic ions and neutral molecules are an alternative source of hydrocarbon ions. It is instructive to compare the relative abundances of the ions at different reduced current densities, $J/n^2$. The effect of reducing $J/n^2$ is to increase the probability of ion-molecule interaction, which results in the production of fragment hydrocarbon ions. As $J/n^2$ is decreased, the current carried by $\text{C}^+$, $\text{CH}^+$, $\text{CH}_2^+$ and $\text{CH}_3^+$ ions increases at the expense of the $\text{H}^+$, $\text{H}_2^+$ and $\text{H}_3^+$ ions (as illustrated in Figure 4) whilst the current of $\text{CH}_4^+$ ions does not significantly change. As there is a much larger reduction in the abundance of the $\text{H}^+$ ion compared with the $\text{H}_2^+$ and $\text{H}_3^+$ ions upon the introduction of $\text{CH}_4$ into the discharge (compare Figures 2 and 3) it would appear that hydrocarbon ions are produced primarily by collision between $\text{H}^+$ ions and neutral $\text{CH}_4^+$ molecules.

6. CONCLUSIONS

Energy spectra have been measured at the cathode of a glow discharge in 5% methane 95% hydrogen atmosphere at pressures between 1 torr and 6 torr and at current densities between 2.4 Am$^{-2}$ and 26 Am$^{-2}$. A significant current of hydrocarbon ions is observed at large fractions of $V/V_c$. Approximately 75% of the ionic current at the cathode is carried by hydrocarbon ions with some 19% of the ion current carried by higher hydrocarbons, predominantly those with 2 carbon atoms. Resonant charge transfer collisions are of minor importance in determining the energy of ions at the cathode. The large abundance of hydrocarbon ions cannot be explained by electron ionisation of methane. Fragment hydrocarbon ions are produced predominantly by the interaction of hydrogen ions with methane molecules in the dark space.

7. REFERENCES

Figure 2. Energy of ions at cathode of 100% H₂ discharge

Figure 3. Energy of ions at cathode of 5% CH₄ 95% H₂ discharge

Figure 4. Distribution of ionic current

Figure 5. Schematic diagram of the apparatus

Normalized ion current (mA)

 Ion energy expressed as V/Vc

Normalized ion current (mA)

 Ion energy expressed as V/Vc

Reduced current density × 10⁻³ (A/m²)