Atmospheric Plasma Analysis by Molecular Beam Mass Spectrometry

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Introduction

The use of atmospheric plasmas is growing in interest due to their advantage in processing materials, mainly organic, which are not suitable for high vacuum. Such discharges are commonly studied by optical emission spectroscopy but, to understand the surface properties of the treated material, it is important to know the energy and identity of the impinging species.

Atmospheric discharges from a number of gas mixtures have been studied using a Hiden EQP mass/energy analyser. The discharges were generated by a radio frequency driven atmospheric plasma source and sampled using a multi-stage differentially pumped molecular beam inlet system. Results for gas mixtures containing different percentages of O_2, N_2, N_2O and CO_2 in Helium are compared.

Energy distributions of the ionic species are reported as a function of the discharge power and distance between the plasma source and the entrance to the analyser.

Additionally, the pathways for producing radical species in the various mixtures were identified by electron attachment and appearance potential methods.

Experiment

(i) Discharge

The discharge was generated by a radio frequency driven atmospheric plasma source, based upon the design of Stoffels et al [1]. This original design was adapted to include a second, concentric gas inlet in order to study mixtures of gases. The inner gas inlet delivers helium to the plasma volume and the outer gas inlet carries different percentages of the gas to be studied (oxygen, nitrogen, nitrous oxide and carbon dioxide). The low power discharge, around 7W, was produced between the plasma source and the entrance of the Molecular Beam Mass Spectrometer (MBMS) analyser as shown in Figure 1.

(ii) Diagnostics

Species created in the atmospheric discharge were sampled using a triple stage differentially pumped molecular beam inlet system and subsequently detected with the Hiden EQP mass/energy analyser. A schematic of the arrangement is shown in Figure 2. The EQP mass/energy analyser is housed in a vacuum chamber with a further two intermediate expansion chambers between it and the plasma. Each of these three chambers, or stages, are separated by aligned skimmer cones and continuously pumped by separate turbo molecular pump sets. Due to the free expansion from atmospheric pressure to the lower pressure stages a molecular beam is formed and plasma species are sampled and detected without undergoing further reactions.

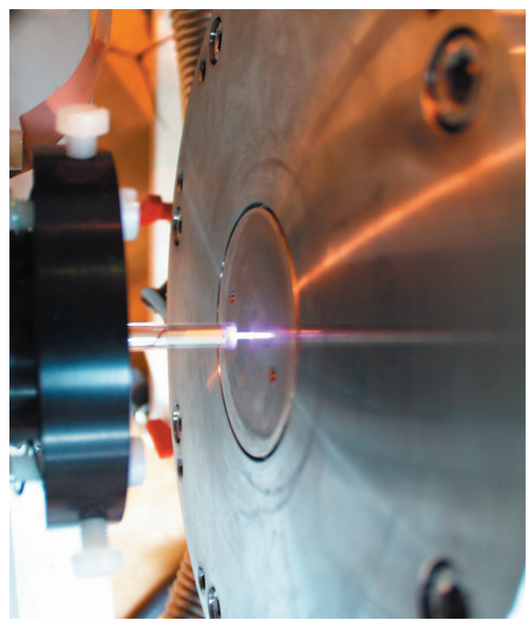

Fig 1. Atmospheric plasma produced between the RF electrode, or needle, and the sampling orifice of the Hiden Molecular Beam Mass Spectrometer.

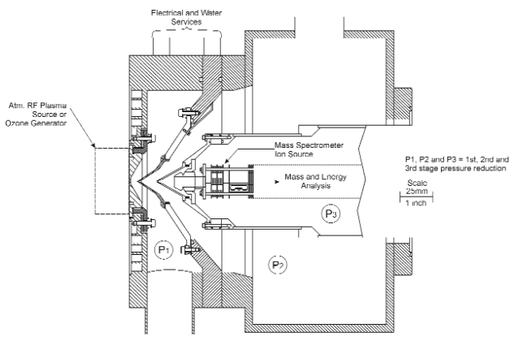

Fig 2. Schematic of the Hiden Modulated Beam Mass Spectrometer System. The three cones are fitted with apertures of 0.2mm at the first stage, 0.3mm at the second stage and 1.0mm at the entrance of the EQP mass/energy analyser.

Ions

Figure 3 shows a representative positive ion spectrum from a He(75%)/O_2(25%) discharge. The discharge was produced at low power (5W) and at a distance of 4mm from the MBMS sampling orifice.

The addition of oxygen produced a high percentage of dissociated O^+ ions. Other species observed included HeH^+, NO^+ and also H_3O^+ formed from atmospheric water vapour.

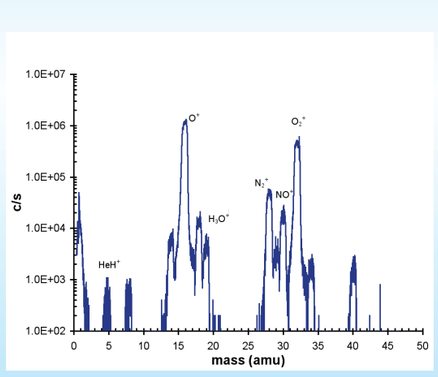

Fig 3. Positive ion mass spectrum.

The effect upon the positive ion energy distribution of varying the distance between the discharge electrode and the grounded sampling orifice plate is shown in Figure 4. The discharge conditions were He(75%)/N_2(25%) at 7W input power.

The ion energy distributions are similar with the peak in the energy distribution increasing slightly as distance is reduced. The optimum distance was found to be 4mm. At distances closer than this the discharge became unstable. A similar result is observed for different percentage gas mixtures.

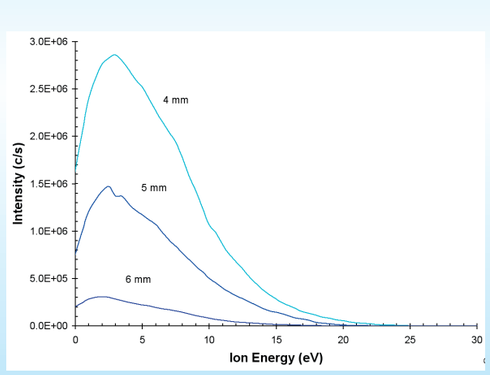

Fig 4. Ion energy distributions for N^+ from the He/N_2 plasma as a function of distance from the sampling orifice.

The ion energy distribution (O^+ ions) was also measured as a function of discharge power as shown in Figure 4. The discharge conditions were He(75%)/O_2(25%) at a distance of 4mm.

As the applied power is increased the plasma potential, which is around 1-2V at 3W, increases and more energetic ions are observed with the tail of the distribution extending to almost 50eV at 10W.

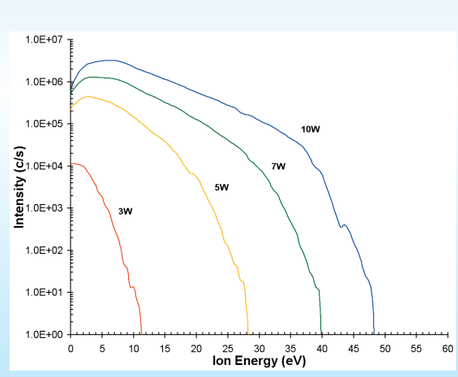

Fig 5. Ion energy distributions for O^+ from the He/O_2 plasma as a function of discharge power.

Neutrals

By utilising the internal ioniser and ion optics of the EQP instrument the neutral plasma particles can be studied and charged particles can be rejected. The spectrum is a convolution of the neutrals sampled from the plasma and the background neutrals ionised in the internal ionisation source of the EQP.

Figure 6 shows the mass spectra for a He/O_2 discharge when the plasma is on and when it is off. The difference in these spectra can be interpreted to provide information on the sampled neutrals.

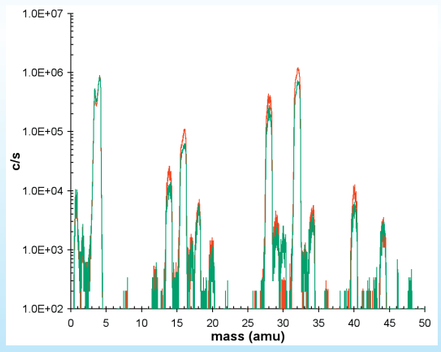

Fig 6. Neutral mass spectra for plasma on (red trace) and plasma off or background (green trace).

Appearance potential measurements are a well established method for quantifying the radical component of a plasma. Figure 7 shows the appearance potential scans for atomic oxygen for both plasma off and plasma on conditions.

The O^+ signal is partly due to direct ionisation of O radicals;

$O + e \rightarrow O^+ + 2e$ (Ei= 14.8 eV)

and partly due to dissociative ionisation of O_2 molecules;

$O_2 + e \rightarrow O^+ + O + 2e$ (Ei=20.3 eV)

With the plasma off, the background O radicals are generated through dissociation of O_2 on the ioniser filaments.

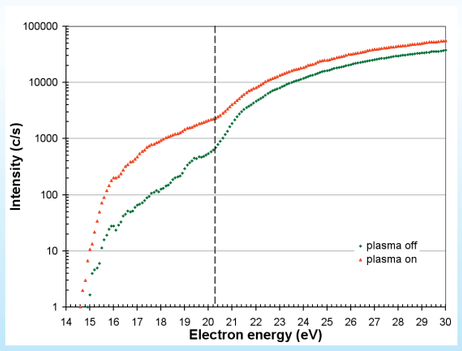

Fig 7. Appearance potential scans for O with the plasma on and off. The threshold for the dissociative ionisation of O_2 is 20.3eV.

The equivalent appearance potential scans for N, from a He/N2 mixture, are shown in Figure 8 and correspond to the processes;

$N + e \rightarrow N^+ + 2e$ (Ei= 16.5 eV)

and dissociative ionisation of N2;

$N_2 + e \rightarrow N^+ + N + 2e$ (Ei=25.2 eV)

Similar measurements have been recorded for other radicals from industrially relevant gas mixtures (e.g. NOx from He/N_2O) and the quantification of these results will be the subject of further work.

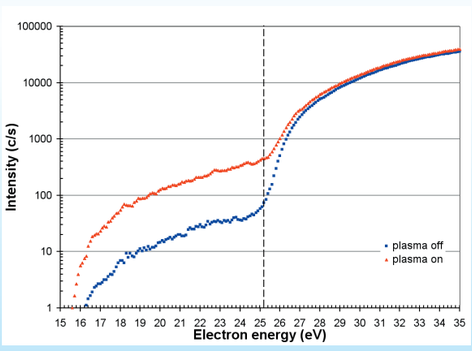

Fig. 8. Appearance potential scans for N with the plasma on and off. The threshold for the dissociative ionisation from N_2 is 25.2eV.

Ozone

Ozone produced by atmospheric plasma sources is widely used as a sterilising agent. The Hiden MBMS system has been used to make preliminary measurements of ozone produced from one such commercial source (Enaly Trade Co. Ltd.).

O^+, O_2^+ and O_3^+ ions were observed. The appearance potential of O_3^+ (at around 10ppm) was measured at 12.2 eV, Figure 9. This is in agreement with the values reported by Radwan et al. [2].

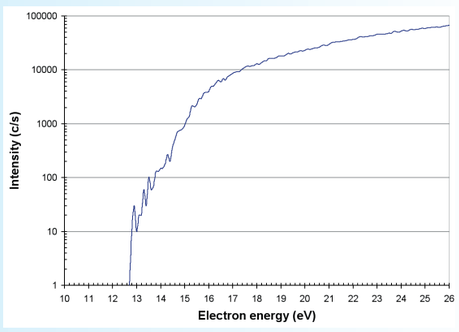

Fig 9. Appearance potential of O_3^+ produced in a commercial ozone generator.

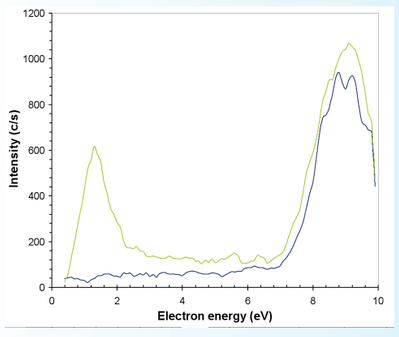

Fig. 10. O_2^- produced by electron attachment in the EQP ion source when the ozone generator is on (green line) and when it is off (blue line).

The internal ionisation source of the EQP mass/energy analyser may also be set to operate at low electron energies in order to study electron attachment processes. The electron attachment scans for the production of O_2^- are shown in Figure 10 when the ozone generator is on and off. For both cases there is a large attachment peak between 8-10eV which is from direct attachment to O_2.

When the ozone generator is switched on a second, smaller attachment peak is seen around 1.5eV which is due to the dissociative attachment process;

$O_3 + e \rightarrow O_2^- + O$ (Ea= 1.5 eV),

in agreement with previously reported results, Curran [3].

Conclusions

The Hiden Molecular Beam Mass Spectrometer System and EQP mass/energy analyser have been used to study various atmospheric plasma sources pertinent to materials processing.

Positive ions have been identified and their energy distributions measured. Various radicals have been identified by appearance potential and electron attachment mass spectrometry. Further work will concentrate on quantifying the preliminary data presented here.

References

[1] E Stoffels, A J Flikweert, V W Stoffels and G M W Kroesen, Plasma Sources Sci. Technol, 11 (2002) pp 383-388

[2] T N Radwan and D W Turner, J. Chem. Soc. (A), (1966) pp 85 – 86

[3] R K Curran, J. Chem. Phys., V(35) 5 (1961) pp 1849-1851