Low-pressure DC discharge in vapour of Methanol and Ethanol

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In this work we present measurements of Volt-Ampere (*V-A*) characteristic of discharges in methanol and ethanol vapours for the conditions in the left-hand branch of Paschen curve at *pd* (pressure times electrode gap) of 0.15 Torr cm and *d* = 1.1 cm. Along with *V-A* measurements we recorded axial emission profiles of light using an ICCD camera. Profiles reveal influence of heavy particle processes in gas excitation and ionisation. Spectrally resolved measurements of spatial profiles are also performed with optical filters which are transparent at wavelengths 431 nm and 656 nm. It is shown that dominant part of emission in discharges of methanol and ethanol vapour stems from excited hydrogen atoms and CH radicals.

1. Introduction

The field of discharges in liquids/vapours of liquids, especially organic ones, become important area for developing of applications. A wide applicability range of discharges in simplest alcohols (methanol, ethanol), from nanotechnology, for nanographene synthesis and fast growth of carbon nanotubes [1,2] to fuel industry for hydrogen production [3], make these discharges interesting for research. Therefore, further development of novel and improvement of existing applications require understanding of elementary processes which occur in these discharges.

For resolving of complicated phenomena which are taking place in liquid and vapour discharges it is necessary to obtain relevant experimental data. Since majority of applications work in glow discharge regime, it is important to comprehend electrical characteristics of discharges. Moreover, in order to analyse the secondary electron production and develop realistic models of discharges it is not sufficient to model only the Paschen curve, but also the Volt-Ampere characteristics of discharge [4].

Thus, in this work we present Volt-Ampere characteristics of methanol and ethanol vapour discharges measured at working conditions in the left-hand branch of the Paschen curve. Electrical measurements are supported with recordings of axial discharge structure by an ICCD camera. Hence, our study of low-pressure discharges in alcohol vapour that started with examination of breakdown conditions [5] continued with the investigation of electrical and optical properties of the discharge sweeping through the Volt-Ampere characteristics in wide range of currents.

2. Experimental set-up

The experimental set-up used for measurements is shown in Figure 1. The discharge is ignited in a plan-parallel electrode system placed inside a tight quartz tube, to prevent long-path breakdown. The copper cathode and quartz anode coated with transparent and conductive thin platinum film, are located at distance *d* of 1.1 cm. The diameter (2r) of electrodes is 5.4 cm. The vapours are obtained from 99% methanol and 95% ethanol, using the same preparation procedure as earlier for water vapour [6].

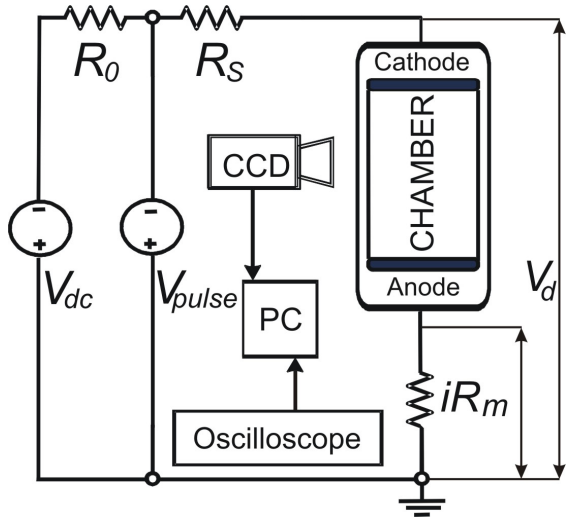

Figure 1. Experimental set-up scheme.

Very reproducible and reliable measurements of Volt-Ampere characteristics are achieved due to the electric circuit which allows applying a pulse of voltage in addition to running discharge at small DC current (~ 1 μA). This small DC current is used to reduce the breakdown delay time, while pulsed regime prevents heating and conditioning of the cathode surface during the measurements [7]. Pulses last long enough to allow formation of steady-state discharge and measurement of constant values in voltage and current signals. During the pulse, axial

emission profiles are recorded by fast sensitive ICCD camera (Andor IStar DH720-18U-03). Obtained emission profiles correspond to a discharge running steadily for a short time (few ms) within the pulse. Emission profiles are acquired integrally, in visual range of spectra and by using optical filters for CH band at 431 nm and Hα line at 656 nm. Spectra of emission are also recorded, by spectrograph ORIEL MS127i with focal length of 138 mm.

More details about the experimental setup and information on measurement technique can be found elsewhere [6,8].

3. Results and Discussion

3.1. Volt-Ampere characteristics

In order to characterize non-equilibrium discharge in several working regimes – low-current Townsend regime, glow and abnormal glow discharge, measurements of Volt-Ampere characteristics were performed in a range of discharge currents from ~1 μA to several mA. *V-A* characteristics were obtained at several different pressures, i.e. *pd* values. In Figure 2 we show plots of voltage and current dependence in methanol (squares) and ethanol (circles) at *pd* = 0.15 Torr cm. Operating regimes typical for low-pressure DC discharges can be clearly distinguished [9].

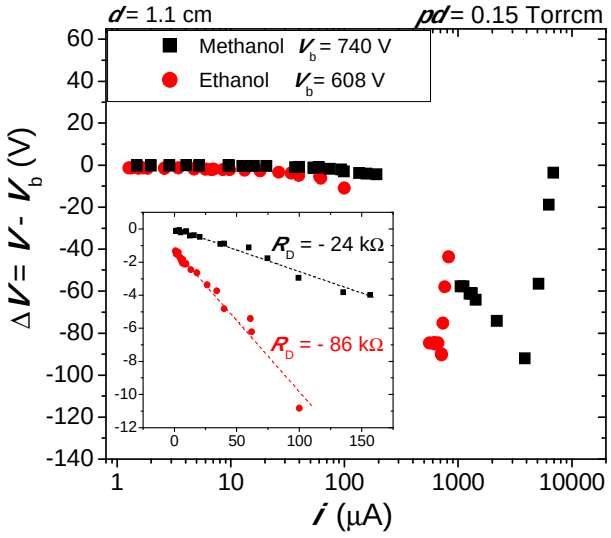

Figure 2. Volt-Ampere characteristics for discharges in methanol and ethanol at *pd* = 0.15 Torr cm and *d* = 1.1 cm. Inset shows low-current region of the *V-A* characteristics.

After breakdown, with sufficiently large resistance in the electrical circuit, discharge runs in Townsend mode. This interval of low currents is zoomed with linear current axis in the inset of Figure 2. In both *V-A* characteristics the discharge voltage is linearly descending with the current increase, with liner fit indicated by dashed lines in the inset. Negative differential resistance is a consequence of space charge effects emerging due to increase of the discharge current [10]. Positive space charge effectively increases the field in front of the cathode, which leads to higher ionization coefficient and secondary electron yield, allowing the discharge to run at lower voltage. In alcohol vapours, experimentally measured differential resistances have value of -24 kΩ in methanol vapour and -86 kΩ in ethanol vapour. These values are similar to the values determined for other molecular gases [11].

With the current increase, in region of transition towards normal glow, regime of free running oscillations occurs. This corresponds to discontinuity interval in *V-A* characteristics which starts at currents of 100 μA for ethanol and around 200 μA for methanol.

At even higher currents, the discharge runs steadily in normal glow regime. In methanol vapours this regime extends to almost 4 mA while in ethanol discharges normal glow ends at around 700 μA. After normal glow, further increase of the discharge current is followed by voltage increase i.e. the discharge operates in abnormal glow regime.

3.2. Spatial profiles of discharge

Our experimental setup enables us to make images of the discharge running synchronized with current and voltage pulses. We followed development of spatial structure of the discharge operating in different modes. In Figure 3 we show 2D images of discharges integrated in the visible region of the spectra for both alcohols.

In Townsend regime discharge is diffuse and occupies almost entire electrode surface, as shown in Figure 3a) for currents ~30 μA. Maximum emission intensity is not near the anode as it is expected for this regime but near the cathode. This is effect of heavy particle processes taking place in the cathode region [8]. In normal glow regime, at currents 716 and 1120 μA in ethanol and methanol vapours respectively (Figure 3b)), the discharge becomes somewhat constricted. Constrictions are much more pronounced at higher *pd*-s [10,12]. With increasing of current, voltage rises and the discharge operates in abnormal regime occupying the entire electrode area (Figure 3c)) and with much higher intensity of emission. As before, the highest peak of total emission is close to the cathode but another smaller one is now visible in front of the anode due

to formation of the cathode fall [7]. The cathode fall is completely formed in abnormal glow and electron-induced emission in the discharge becomes comparable to heavy-particle emission.

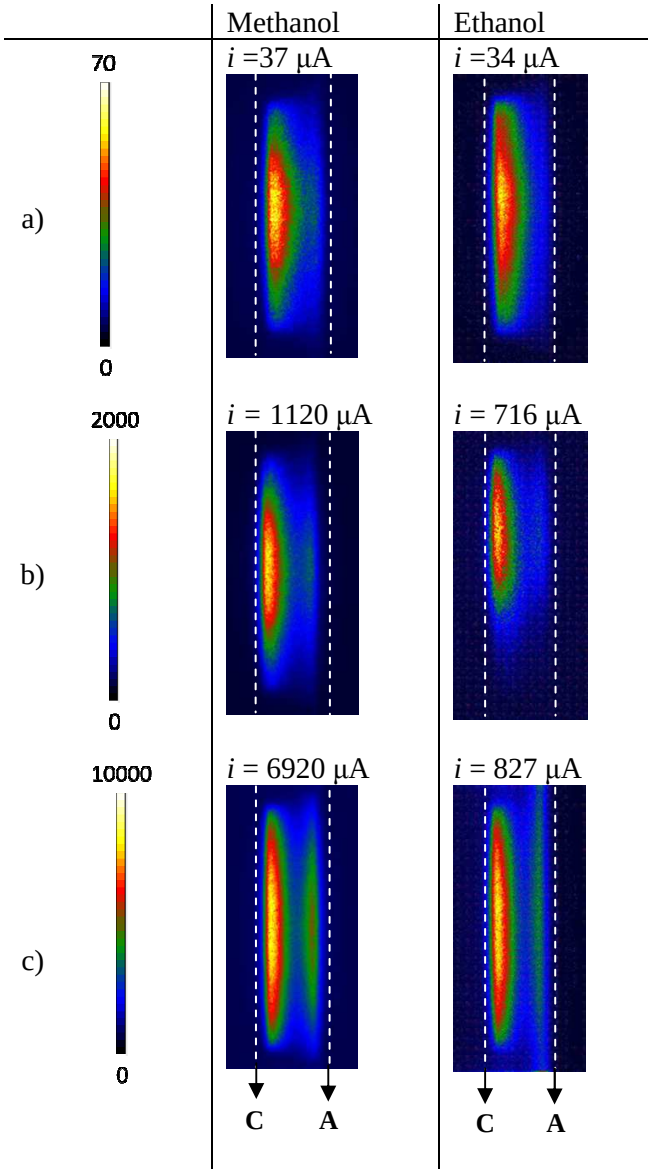

Figure 3. 2D images of discharge in methanol and ethanol vapours for *pd* = 0.15 Torr cm at *d* = 1.1 cm for different discharge regimes: a) Townsend, b) normal and c) abnormal glow.

3.3. Spectrally resolved measurements

Measurement of emission spectra enables identification of species existing in the discharge. In Figure 4 we present optical emission spectrum for methanol vapour discharge recorded at *pd* = 0.15 Torr cm. Emission coming from OH, CHO, CH, Hα and Hβ (Balmer series lines for H atom) are visible in spectral range 300-900 nm. Therefore heavy particles produced in vapour dissociation which participate in processes of collisional excitation and ionization are H atoms and some heavier dissociation fragments (OH and/or CxHy species) [1].

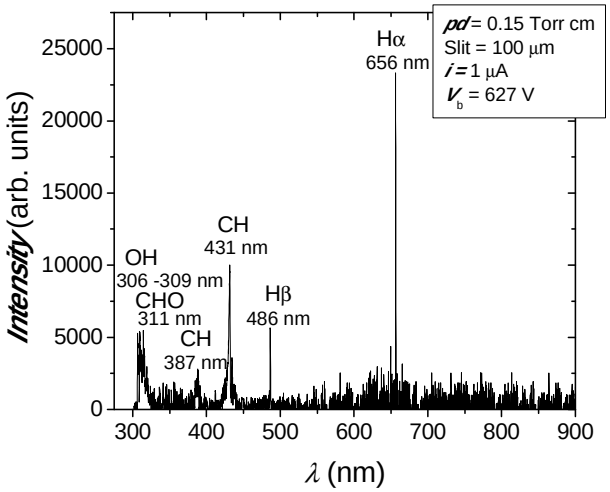

Figure 4. Optical-emission spectrum of methanol vapour discharge at *pd* = 0.15 Torr cm and *d* = 1.1 cm.

As emission is the most intense at 656 nm and 431 nm, we recorded spatial distribution of emission with Hα and CH band pass optical filers.

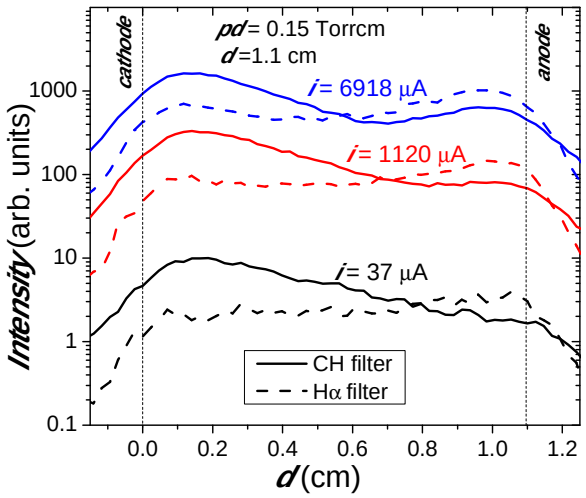

Figure 5. Axial emission profiles of discharge in methanol vapour at *pd* = 0.15 Torr cm and *d* = 1.1 cm with optical Hα and CH filters.

The emission profiles are extracted along the axis of the discharge from 2D images taken with filters. Profiles recorded with optical filter for CH band (Figure 5-solid line) follows the integrated emission profile in shape peaking in front of the cathode. Thus, heavy particles (positive ions and fast neutrals) have significant contribution to excitation of CH radical emitting at this wavelength.

On the other hand, profiles recorded with optical filter for the emission from Balmer excited hydrogen atoms-Hα line (Figure 5 – dashed line) show emission peak near the anode which indicate that for hydrogen atoms greater part of emission comes from excitation induced by electrons.

At high currents peak of emission in anode-region, which corresponds to negative glow, is visible for CH band as well as emission of Hα near the cathode.

4. Conclusion

Considering the fact that many applications that utilize discharge operation in vapours of alcohols work in different discharge regimes, we investigated operating regimes of low-pressure discharges in vapours of methanol and ethanol, from low-current Townsend to high current abnormal glow. Measurements of electrical properties are supported with recording of optical emission spectra and spatial profiles of stable regimes at pd = 0.15 Torr cm. The characteristics have shape anticipated for this type of non-equilibrium discharges. Profiles integrated in visual range and resolved spectrally (using filters) reveal strong emission mostly from CH band (431 nm) in front of the cathode. This emission, originating from heavy-particle processes, is present for all regimes of discharge.

Acknowledgements

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5. References

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