Generation and characterisation of cold atmospheric liquid-containing plasmas

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Generation and characterisation of cold atmospheric liquid-containing plasmas

By

Jingjing Liu

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of
Doctor of Philosophy of Loughborough University

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Abstract

This thesis presents an experimental study of non-thermal atmospheric pressure gas plasmas in presence of liquid as an efficient source of transient and reactive species to initiate chemical reactions necessary for many important applications. Two types of liquid-containing plasmas are considered: discharges formed between a needle electrode and a liquid electrode, and plasma jets formed in a water vapour flow mixed in helium or argon gas. Two plasma modes (the pulsed and the continuous mode) are observed in the needle-to-liquid plasma. A comparative study of the needle-to-liquid plasma in the continuous mode with DC and AC excitations reveals that the plasmas are glow discharges, and AC excited plasmas have the highest energy efficiency. A study of helium/water vapour plasma jet shows that "plasma bullets" are formed even with water vapour in the gas mixture, but become quenched when the moist helium flow rate is above 300sccm (~1800ppm water concentration). Moderate amount of water vapour (~250ppm water concentration) is beneficial for active species production mainly due to the high electron density. Hydrogen peroxide production in saline solution with three different plasma sources is investigated due to the importance of H$_2$O$_2$ in several important applications. Long lifetime of H$_2$O$_2$ in the liquid after plasma treatment indicates an exciting possibility of plasma pharmacy.

Key words: atmospheric pressure gas plasmas, liquid-containing plasmas, needle-to-liquid plasma, helium/water vapour plasma jet, hydrogen peroxide, plasma pharmacy.
First of all, I would like to express my sincere gratitude to my supervisor, Professor Michael G Kong, for his guidance and support throughout my PhD study in Loughborough University. His unremitting encouragement has led me to every challenge with aspiration and excitement in the research of low temperature liquid-containing plasmas. His care goes beyond the supervision of my study, from which I will benefit for my life.

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Publications


6. Liu, J. and Kong, M.G., “Hydrogen peroxide production with He/H_2O jet plasmas”, will be presented at 8th *Technological Plasma Workshop*, Bristol, UK, January 6-7, 2011
Contents

Abstract .......................................................................................................................... I
Acknowledgement ............................................................................................................ II
Publications ..................................................................................................................... III
Contents .......................................................................................................................... IV

Chapter 1 Introduction .................................................................................................. 1
  1.1 Historical review .................................................................................................... 1
  1.2 Gas plasma ............................................................................................................. 3
  1.3 Plasma breakdown ................................................................................................. 5
  1.4 Characteristics of glow discharges ........................................................................ 7
    1.4.1 Low pressure normal glow discharge ........................................................... 7
    1.4.2 Atmospheric pressure glow discharge ......................................................... 8
  1.5 Liquid-containing gas plasmas .............................................................................. 10
  1.6 Organization of the thesis ..................................................................................... 11
  1.7 Contribution of this thesis .................................................................................... 13
References ...................................................................................................................... 15

Chapter 2 Diagnostics methodology ............................................................................ 21
  2.1 Electrical measurement ......................................................................................... 21
  2.2 Nanosecond images by ICCD camera ................................................................... 22
  2.3 Optical emission spectroscopy ............................................................................. 24
    2.3.1 Relative and absolute optical intensity measurement .................................. 25
4.4 Production of active plasma species .................................................. 86
4.5 Summary ......................................................................................... 92
References............................................................................................. 94

Chapter 5 Characteristics of He/H₂O plasma jets ......................... 96
5.1 Introduction ...................................................................................... 96
5.2 Experimental setup .......................................................................... 98
5.3 Electrical characteristics.................................................................. 99
5.4 Nanosecond images in the bullet and arc modes ...................... 102
5.5 Rotational, vibrational and excitation temperatures ............. 106
5.6 Active species and ozone production ........................................... 111
5.7 Discussion of the active species production mechanism ....... 115
5.8 Summary ......................................................................................... 124
References............................................................................................. 125

Chapter 6 Hydrogen peroxide production with different plasma sources .......................................................... 130
6.1 Introduction ...................................................................................... 130
6.2 Experimental setup .......................................................................... 131
6.3 H₂O₂ production with AC needle-saline air plasmas............... 132
6.4 H₂O₂ production with He/H₂O vapour jet plasmas ................. 139
6.5 H₂O₂ production with Ar/ H₂O jet plasmas ................................. 147
6.6 Comparison of H₂O₂ production with different plasmas .......... 154
6.7 Summary .......................................................................................................................... 159

References.......................................................................................................................... 160

Chapter 7 Conclusions and future works ................................................................. 165

7.1 Conclusions .................................................................................................................. 165

7.1.1 Characteristics of needle-water plasmas............................................................... 165

7.1.2 Characteristics of helium/water vapour jet plasmas........................................... 166

7.1.3 Hydrogen peroxide production with three plasma sources ....................... 167

7.2 Future works .............................................................................................................. 168
Chapter 1
Introduction

1.1 Historical review

Plasma is a medium containing many charged particles, governed by electromagnetic forces, and uncharged species. It is a quasineutral gas of charged particles with approximately the same amount of positive and negative charges, and the charges possess collective behaviours. Plasma is the term used in physics to designate the fourth state of matter\(^1,2\) (Fig 1.1). About 99% of our visible universe exists in a plasma state, but normally plasma does not exist naturally on earth. One of the exceptions is during lightning in a thunderstorm. In laboratories, plasma is produced by heating gases to a high temperature or by the electrical discharge at a high voltage. Macroscopically, the plasma medium is described by its temperature and density\(^1,2\) as shown in Fig 1.2.

Fig 1.1 The four states of matter: plasma is referred to as the fourth state.
Chapter 1 Introduction

Fig 1.2 Plasmas classified as a function of their density and temperature.\textsuperscript{1,2}

The scientific study of plasma began with the development of the steady-state DC arc discharge by Sir Humphry Davy in 1808 and with the development of the high voltage DC electrical discharge tube (~1 Torr) by Michael Faraday and others in the 1830s. Plasma was identified as the fourth state of matter by Sir William Crookes in 1879. The word \textit{plasma} was introduced by Irving Langmuir to explain some phenomena occurring in electrical discharges in 1928.\textsuperscript{1,3}

Arc and DC electrical discharge plasmas were extensively researched in scientific laboratories during the 19\textsuperscript{th} century. Plasma research was stimulated during the 1920’s by the development of magnetoionic theory which describes the wave propagation in a cold homogeneous plasma, immersed in a magnetic field. In the 1930’s, commercial research on MHD (magnetohydrodynamic) power generators began in the United States. In the late 1940’s, plasmas were generated by microwave discharges after the development and flourishing of the microwave technology, particularly the magnetron. A major impetus to plasma
physics has been controlled fusion research, which began in the major industrialised countries around 1950 and continues to the present day. Since 1970, low temperature plasmas have been extensively used in the microelectronics industry for the deposition and dry etching processes necessary for the fabrication of microelectronic circuits.\textsuperscript{1.3,1.4}

1.2 Gas plasma

Most early research on electrical discharge physics was performed on the classical low pressure electrical discharge tube illustrated in Fig 1.3. It consists of an evacuated glass tube with one circular disk electrode at both ends, which are then connected to a high voltage DC power supply. The voltage-current characteristics of a DC low pressure electrical discharge are shown in Fig 1.4.

![Fig 1.3 Schematic of the low pressure electrical discharge tube.\textsuperscript{1.3}](image)

The regime between A and E on the voltage-current characteristic is termed the dark discharge region because, except for the corona discharges and the
electrical breakdown spark itself, the discharge remains invisible to the eye. Once electrical breakdown occurs at point E, the discharge undertakes a transition to the glow discharge regime, in which the current is high enough for the plasma to be visible to the eye. After an abrupt transition from the point E to F, the discharge evolves into the normal glow region (from point F to G), in which the voltage across the discharge is almost independent of the current. At the point G, the plasma covers the entire cathode surface, the discharge enters the abnormal glow regime from G through H, in which the voltage increases with the current. If one were to start at the point G of the curve and move to the left, the discharge would maintain itself in the normal glow regime to the point F' instead of retracing the voltage-current characteristic from F to E, and then make a transition back to a regime from point F' to C known as the Townsend regime (see discussion in section 1.3). At the point H, the current density on the cathode

![Voltage-current characteristic of a DC low pressure electrical discharge.](image.png)
becomes sufficiently large to heat the cathode to incandescence and triggers an
abrupt and rapid glow-to-arc transition. The regime of falling voltage with
increasing current between I and J is the non-thermal arc regime, in which the
electron, ion, and gas temperatures are unequal. The portion with positive slope
between J and K is the thermal arc regime, in which the plasma is close to
thermodynamic equilibrium and the temperatures of all species are
approximately equal.

1.3 Plasma breakdown

Plasma breakdown is a fundamental process in gas discharge physics.
Investigations of discharge ignition are almost as old as studies of discharges. In
1889, Paschen performed experiments studying the minimum potential
difference that was needed to create a spark between two electrodes in a glass
tube.\(^1\)\(^5\) It was found that this voltage depended on the gas type, the pressure in
the tube \(p\), and the separation of the electrodes \(d\) as described in the
following equation:

\[
V = \frac{a(pd)}{\ln(pd) + b} \quad (1.1)
\]

where parameters \(a\) and \(b\) are determined by the properties of the gas.

The minimum breakdown voltage is a function of the product between
pressure and gap distance, \(pd\). The breakdown voltage as a function of pressure
times gap size is shown in Fig 1.5, commonly known as the Paschen curve.\(^1\)\(^6\)\(^1\)\(^7\)

In 1909, Townsend proposed a theory that could explain the observed
breakdown phenomena.\(^1\)\(^8\) This theory gives an accurate description of the
breakdown process for a set of conditions in which the product \(pd\) is limited to a
range of about 0.1-100 Pa m and the electrode geometries are relatively simple
Chapter 1 Introduction

The electrons initially produced in the creation of ion-electron pairs by ionising radiation or from other sources are accelerated in the electric field of the discharge tube. If the electric field is high enough, the electrons can acquire sufficient energy before reaching the anode and so can ionise one or more gas atoms or molecules. When electrons reach the anode, their kinetic energy deposited onto the anode can induce electron emission from the anode material. In addition, secondary electrons are emitted from the cathode upon impact of energetic ions, metastables and photons. As the electric field becomes stronger, these secondary electrons may themselves ionise more gas atoms or molecules, thus leading to a chain reaction, or an avalanche of electron and ion production. This is the Townsend discharge region between C and E in Fig 1.4.

In the 1930’s and 1940’s, new observations of plasma breakdown under specific conditions showed features that were not in agreement with the

![Paschen curves for helium, neon, argon, hydrogen and nitrogen.](image)
Townsend theory. Discharges at high pressures and long electrode gaps developed much faster than what could be explained using the conventional Townsend breakdown theory. At high gas pressure, above about 100 Torr, the mechanism of electrical breakdown often involves streamer formation from the anode. This streamer breakdown theory was developed by Loeb, Meek, and Raether, in which space charge effects inside electron avalanches were taken into account.

1.4 Characteristics of glow discharges

1.4.1 Low pressure normal glow discharge

The glow discharge is a self-sustaining discharge with a cold cathode emitting secondary electrons mostly due to positive ion bombardment. The plasma which forms in a classical DC low pressure electrical discharge in the normal glow regime can have an appearance as shown in Fig 1.6. These structures were first observed in the 1830’s by Michael Faraday, and later by such early investigators of the low pressure electrical discharge tube as M Abria (1848).

Most of the potential drop across the electrodes is concentrated in a layer close to the cathode, known as the cathode fall. The thickness of the cathode fall
layer is inversely proportional to the density (pressure) of the gas. If the inter-electrode separation is sufficiently large, an electrically neutral plasma region with fairly weak electric field is formed between the cathode layer and the anode. Its relatively homogeneous middle part is called the positive column, in which there is a slowly increasing potential, resulting in an approximately constant, low electric field. In contrast to the cathode layer, whose existence is vital for the glow discharge, the positive column is not an essential part. No such column is formed if the cathode layer fills the inter-electrode gap. However, if the distance is insufficient for the formation of the required cathode layer, the glow discharge cannot be ignited. Finally, in front of the anode, there is a small potential jump due to the anode sheath which has a negative space charge due to electrons travelling from the positive column to the anode and a higher electric field than the positive column.\textsuperscript{1.3,1.7}

1.4.2 Atmospheric pressure glow discharge

Atmospheric pressure glow discharges (APGD) have attracted a great deal of attention in recent years due to their ability to discard the need for a vacuum chamber. As the gas pressure is raised, the number of atoms/molecules increases proportionally and consequently more electron collisions occur and the ionisation rate increases significantly. At atmospheric pressure, it is often difficult to maintain a stable discharge as the high breakdown voltage combines with high gas density to lead to rapid ionisation, considerable heating and even a glow-to-arc transition. To generate stable APGD, helium gas is commonly used as the working gas. It is selected due to its low breakdown voltage and stability comparing to other gases.\textsuperscript{1.14}
Chapter 1 Introduction

To prevent the APGD from evolving into an arc, one solution is to control the growth of the discharge current by adding one or two dielectric barriers to the electrodes\textsuperscript{1.15-1.18} or using the resistive electrodes\textsuperscript{1.19-1.21} Alternatively the electrode gap can be reduced to a sub-millimetre scale and the resulting micro-plasmas may be sustained in a glow discharge mode at a very wide frequency range from DC\textsuperscript{1.22,1.23}, kilohertz frequency\textsuperscript{1.24}, radio frequency (RF)\textsuperscript{1.25} and microwave\textsuperscript{1.26} The glow-to-arc transition can also be mitigated by flowing the carrier gas in a small channel, and the resulting plasmas are known as plasma jets\textsuperscript{1.27,1.28} APGD produced with dielectric barrier layers is called dielectric barrier discharge (DBD). In this kind of discharge, streamers can be avoided when the electric field is below the Meek criterion\textsuperscript{1.29} and the discharge operates in the Townsend regime. Secondary electron emission from the dielectric surfaces, which sustains the Townsend regime, relies upon absorbed electrons (with binding energy only about 1eV) that were deposited during a previous DBD excitation cycle. If enough electrons in the electrode gap “survive” the voltage switching time without recombining, they can trigger a transition to the homogeneous mode of the DBD.

The discharge employing a pair of resistive electrodes is known as the resistive barrier discharge (RBD). The RBD can be operated with DC or AC (60Hz) power supplies and is essentially a DBD configuration, where the dielectric barrier is replaced by a highly resistive sheet (few MΩ/cm) covering one or both electrodes\textsuperscript{1.29} The highly resistive sheet plays a role of a distributed resistive ballast, which prevents high currents and arcing.

The RF atmospheric glow discharge or atmospheric-pressure plasma jet (APPJ)\textsuperscript{1.30} is one of the most developed APGD systems. The APPJ can be
Chapter 1 Introduction

sustained in a planar and coaxial system with an electrode gap of a few millimetres, and often at 13.56MHz. In most APPJ configurations, electrodes are not covered by any dielectric material. At atmospheric pressure and microscopic sizes (below 1mm), the glow discharge can be stabilised due to the decrease of $pd$. The breakdown voltage can be kept low, if the electrode separation is reduced when the pressure is increased. Another factor contributes to the stability of atmospheric pressure micro-plasmas are the high losses of charge carriers to the surrounding walls.\textsuperscript{1,31}

1.5 Liquid-containing gas plasmas

The study of electrical discharges in the presence of liquid spans almost 100 years. The large number of journal papers and conference contributions published during the last few years on non-thermal atmospheric pressure plasmas in and in contact with liquids highlights a renewed interest in this particular field of plasma physics and chemistry. Such plasmas involve both gas and liquid phases which add significant complexity compared to gas plasmas.

Various types of non-thermal atmospheric plasmas can be generated in the presence of liquid, examples of which are listed below:

(1) discharges generated inside gas bubbles in an aqueous medium with the bubbles formed via vaporisation and/or external injection,\textsuperscript{1,37,1,38}

(2) discharges formed inside externally supplied gases bubbling through a liquid,\textsuperscript{1,39,1,40}

(3) simultaneous discharges in both gas and liquid phases,\textsuperscript{1,41,1,42}

(4) gas phase discharges over a liquid surface,\textsuperscript{1,43}

(5) gas phase discharges with liquid water droplet sprays.\textsuperscript{1,44}
These systems have several common characteristics including the generation of intense UV radiation, shock waves, active radicals and atomic (e.g. H, O) and molecular (e.g. ·OH, HO₂, H₂O₂, O₃, H₂, O₂) species. These active species are primarily responsible for initiating chemical reactions necessary for many important applications. Examples of commercially successful applications are arthroscopic surgery¹,⁴⁵ and lithotripsy for kidney stone treatment.¹,³⁴ Other interesting and potentially new applications of liquids in contact with plasma include biomedical applications such as wound healing and disinfection,¹,⁴⁶ synthesis of nanoparticles,¹,⁴⁷ plasma assisted combustion,¹,⁴⁸ microsensors for analysis of chemical composition in liquids,¹,⁴⁹ and polymer surface treatment.¹,⁵⁰ Plasmas formed in water with microwave and high frequency sources are also under investigation for chemical synthesis and pollution control.¹,⁵¹,⁵²

1.6 Organization of the thesis

In this thesis, an experimental study of non-thermal atmospheric gas plasmas in presence of liquid is presented. Two types of liquid-containing plasmas are considered: discharges formed between a needle electrode and a liquid electrode, and a needle-ring DBD jet. Following the introduction in Chapter 1, Chapter 2 describes electrical and optical diagnostics methods for plasmas as well as a fluorescence spectroscopic method for measuring hydrogen peroxide concentration, and a chemical method to measure ozone production.

In Chapter 3, electrical and optical characteristics of a needle-to-liquid plasma are investigated. Two plasma modes (the pulsed and the continuous modes) are observed from nanosecond images. In the pulsed mode, plasmas are in general not continuous and extinguish when the voltage changes its polarity. In the
continuous mode on the other hand, the plasma is more intense and always exists in the discharge gap. It is shown that the presence of the plasma influences water properties such as pH, conductivity and temperature due to chemical reactions.

Chapter 4 details a comparative study of the needle-to-liquid plasma in the continuous mode with DC and AC excitations. All plasmas studied are shown to be glow discharges. This study is based on measurements of several key parameters including electrical energy, optical emission intensities of active species, rotational and vibrational temperatures, and the temperatures of the needle and liquid electrodes. AC excited plasmas are shown to have the highest energy efficiency for the production of reactive oxygen species.

Chapter 5 provides a detailed characteristic of helium/water vapour jet plasmas. A needle-ring DBD plasma jet is considered. Voltage and current characteristics are used to reveal four different plasma modes. Water vapour concentration in the gas mixture is shown to significantly influence the plasma modes, and their characteristics such as rotational, vibrational and excitation temperatures, the electron density and the active species generation. The mechanism of active species production is discussed.

Chapter 6 presents a focused study of the production of hydrogen peroxide production in saline solution with different plasma sources. This is motivated by the importance of $\text{H}_2\text{O}_2$ in several important applications. Hydrogen peroxide concentration, production rate and energy efficiency are either measured or calculated. Finally, Chapter 7 discusses the conclusion and future works.
1.7 Contribution of this thesis

The key contributions reported in this thesis can be summarised in the following four areas:

1. Characteristics of AC excited needle-to-liquid plasmas:

The work detailed in Chapter 3 reveals two modes of AC excited plasmas in contact with liquid. The extent of details presented is much more than what has been reported in the literature, and this has added an important contribution to the current understanding of the needle-to-liquid plasmas. In particular, the presence of two plasma modes has not been reported before.

2. Comparison of DC and AC excited needle-to-liquid plasmas in the continuous mode:

Such a comparison has never been reported in literature, but is very useful for understanding the much-less studied AC excited needle-to-liquid plasmas in comparison with their DC counterparts.

3. Characteristic study of helium/water vapour jet plasmas:

Atmospheric plasma jets in He/H\textsubscript{2}O flow are relatively new low-temperature discharges. This work provides a first study and reveals the presence of four different modes. The characteristics change significantly in different modes. Electron density is shown to play a significant role in producing the active species.

4. H\textsubscript{2}O\textsubscript{2} production in three different plasma sources:
All liquid-containing non-thermal atmospheric plasmas are known to produce \( \text{H}_2\text{O}_2 \), a reactive plasma species that is very important to several important applications. However, it has not been clear previously how different plasma sources may fare in terms of their ability to produce abundant \( \text{H}_2\text{O}_2 \). This work offers a quantitative analysis.
Chapter 1 Introduction

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Chapter 1 Introduction


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Chapter 2
Diagnostics methodology

This Chapter presents a detailed discussion of various plasma diagnostic methodologies required for the experimental studies presented in this thesis. These include electrical, optical, fluorescent and chemical techniques, when and where appropriate, relevant theoretical bases for some of these techniques are also presented.

2.1 Electrical measurement

Voltage and current waveforms are recorded by the voltage and current probes, and an oscilloscope with their connection to different experimental setups shown in Fig 2.1. The voltage waveforms of the three plasma sources are recorded by a Tektronix P6015A wideband high voltage probe which is connected to a Tektronix TDS5054B digital phosphor oscilloscope. The current waveform of the AC-excited needle-liquid plasma is measured by a Pearson current monitor (Model 2877) with a coaxial cable connected to the oscilloscope. Since the Pearson probe does not operate below ~300Hz, a Tektronix P2220 voltage probe with a small resistor is used to record the current waveforms for the DC-excited needle-liquid and helium/water vapour jet plasmas. Usually, there
is a 10 ns phase delay between voltage and current waveforms on the oscilloscope due to a finite section of electric circuit between the voltage and current probes. For experiments reported here, the highest driven frequency is 20 kHz, at which a 10 ns delay represents a phase delay of 0.07º. Therefore, it will have negligible effects on the calculation of dissipated electrical power.

Fig 2.1 Connection of voltage and current probes to three plasma sources: (a) an AC-excited needle-liquid plasma, (b) a DC-excited needle-liquid plasma, (c) a plasma jet in helium/water vapour flow.

2.2 Nanosecond images by ICCD camera

In order to investigate the appearance of the plasma discharge and its temporal evolution, time-integrated and time-resolved images are very useful. These are taken by an Andor iStar 720 Gen III intensified CCD camera (Fig 2.2) with an external trigger signal (BNC Digital Delay Generator 7075). The external trigger is used to take image at a precise time point of the applied voltage trace. This camera has a fibre-coupled system that includes a digital delay generator, built into the head. This system is designed for low-light spectroscopy applications requiring fast gating. Its 1024 x 256 array has a 4:1 aspect ratio making it ideally suited to use with an imaging spectrograph such as the Andor Shamrock 303i. A wide selection of photocathode options provides a range of
solutions, either a broad spectral response or optimization in a particular wavelength region.

Fig 2.2 Andor iStar 720 Gen III intensified CCD camera.

An example of time-integrated and time-resolved images\(^1\) taken by this camera is shown in Fig 2.3. It is clear that the time-integrated image shows the general appearance of a plasma jet and the time-resolved images reveal its bullet-like structure on a nanosecond scale. The optical intensity at each pixel (26μm×26μm) of these images can be read in the camera software which gives a spatial-resolved optical intensity profile (Fig 2.3 (c)).

Optical band-pass filters (Thorlabs FWHM (full width at half maximum) 10nm) can be placed in front of the ICCD camera lens to transmit light from plasmas over a particular range of emission wavelengths while blocking the remainder of the plasma emission spectrum. This combination is effective for taking wavelength-resolved images and for investigation of the time-, space- and wavelength-resolved optical emission of plasmas\(^2\)
Fig 2.3 Time-integrated (1ms exposure time) (a) and time-resolved (1ns exposure time) (b) images by Andor iStar 720 Gen III intensified CCD camera and the maximum optical intensity of the plasma bullet as a function of the distance from the exit of dielectric tube (c). (from ref 2.1).

2.3 Optical emission spectroscopy

Langmuir probes are a powerful tool commonly used for the determination of important plasma parameters such as excitation temperature.\textsuperscript{2,3} Currently this technique is most widely used for low temperature, low pressure (less than 0.5 Torr) plasmas, because these conditions satisfy the basic assumptions for the theory of Langmuir probe:\textsuperscript{2,4} (1) the probe only collects charged particles, the colliding particles do not contribute to secondary electron emission; (2) the mean free path is essentially larger than the Debye length so that no collision occurs in the space charge region around the probe; (3) the probe size is small compared
to the Debye length. For atmospheric pressure plasmas, the probe size is larger than the Debye length and the latter is larger than the mean free path\(^2.4\) (usually on a scale of a few tens of nano-meters\(^2.5\)). This is very different to the conditions of low pressure plasmas, and it means that a local plasma may form at the tip of an inserted Langmuir probe. Many efforts as described in ref 2.4 have been attempted to improve the theory of Langmuir probes for atmospheric pressure plasmas. However, these developed theories are at present very complicated with various restrictive assumptions. These make the Langmuir probes inappropriate in general use for non-thermal atmospheric pressure plasmas. As a result, non-invasive techniques are preferred and these are typically optical techniques.

On the other hand, optical emission spectroscopy (OES) is a non-invasive spectroscopic technique that examines photon fluxes emitted by atoms or molecules, as a function of the emission wavelength, during their transition from an excited state to a lower energy state. Each transition of an excited atom or molecule is associated with emission at a characteristic set of discrete wavelengths according to the electronic structure of the atom or molecule. By observing emission at these wavelengths, the elemental composition of the plasma can be determined. OES is a convenient and non-intrusive way to study gas plasma. Since optical intensity is related to the amount of an excited atom or molecule, it can be used to represent the production of plasma species. Plasma parameters such as rotational, vibrational, excitation and electron temperatures and electron density can also be obtained by optical emission spectra.\(^2.6\)
2.3.1 Relative and absolute optical intensity measurement

Relative and absolute optical intensities are useful for the characterisation of excited plasma species. Relative optical intensity gives an indication of different plasma species and their relative production by a given plasma source. Absolute optical intensity is useful for comparison of the production of a particular plasma species with different plasma sources. An Ocean optics USB650 Red Tide spectrometer and an Andor Shamrock SR-303i with Andor iStar 720 Gen III intensified CCD camera are used in this thesis to detect the absolute and relative optical intensities of plasmas.

![USB650 Red Tide spectrometer](image-a) ![LS-1 Tungsten Halogen light source](image-b)

Fig 2.4 (a) USB650 Red Tide spectrometer; (b) LS-1 Tungsten Halogen light source.

The USB650 Red Tide spectrometer (Fig 2.4 (a)) has a wavelength range of 350-1000nm and utilises a detector with 650 active pixels. It is configured with a 25μm entrance slit and offers ~2.0nm optical resolution (FWHM). The relative intensity of an emission spectrum between 350nm and 1000nm can be obtained directly at one time via the SpectraSuite Spectroscopy Operating Software. A LS-1 Tungsten Halogen light source (Fig 2.4 (b)), which has a known absolute spectral output as shown in Fig 2.5, is adopted to calibrate the absolute spectral intensity of the USB650 spectrometer. Then the absolute optical intensity of spectra are acquired usually in the unit of μW/cm²/nm.
Fig 2.5 Absolute spectral output of the LS-1 Tungsten Halogen light source.\textsuperscript{2,11}

The Andor Shamrock SR-303i imaging spectrograph (Fig 2.6 (a)) is designed for rugged, high-performance operation and versatility. Its scan range is from 180nm to 1100nm and its wavelength resolution is <0.2nm. It features an automated, interchangeable triple grating turret (Fig 2.6 (b)) for extended spectral coverage. Grating position 1, 2 and 3 determines three gratings: 600, 1200 and 2400 lines/mm with 72%, 81% and 73% peak efficiency respectively. Relative intensity spectra are obtained via the Solis software with the interface as shown in Fig 2.7 which allows control of many spectrograph functions including wavelength selection, slit control, shutter control, filter selection, exit ports selection and grating selection. In contrast to the Ocean optics USB650 Red Tide spectrometer, the Andor spectrograph allows spectra to be obtained in a narrow wavelength range with high resolution: 142nm wavelength range with grating 1, 66nm with grating 2, and 27nm with grating 3. Absolute optical intensity of spectra is not possible with this spectrometer because it is yet to be properly calibrated.
2.3.2 Rotational and vibrational temperature measurement

Non-thermal plasmas are usually characterised by their rotational temperature ($T_{\text{rot}}$), vibrational temperature ($T_{\text{vib}}$), excitation temperature ($T_{\text{exc}}$) and electron temperature ($T_{\text{e}}$). For non-thermal atmospheric plasmas, their rotational temperature may be used to approximate the gas temperature.\textsuperscript{2,12,2,13} In non-thermal atmospheric plasmas created by externally applied electric fields,
typically $T_e > T_{vib} > T_{rot}$. It is well known that the OH band (transition $A^2\Sigma^+, \nu=0 \rightarrow X^2\Pi, \nu'=0$) between 306-312nm and the N$_2$ C-B band (second positive system) in 360-380nm are often used for measurement of rotational and vibrational temperatures. They are obtained by fitting the measured spectra with a numerically simulated spectra obtained from public-domain software Lifbase and Specair respectively.

An example of the rotational temperature obtained through OH band in Lifbase is shown in Fig 2.8. It is clear that rotational temperature can be obtained by fitting the entire OH band. From Fig 2.8, it is indicated that the intensity peak at 309.1nm is not sensitive to the change of temperature. It works as the reference intensity. Peaks at 307.1nm and 308.2nm are quite sensitive to the variation of rotational temperatures.

![Fig 2.8 Measured and simulated optical emission spectra around the OH line at 309nm for the submicrosecond pulsed atmospheric argon plasma jet.](image)

An example of the rotational temperature obtained through N$_2$ band in Specair is shown in Fig 2.9. In this case, a slit function with a trapezoid of base
0.66nm and top 0.22nm is used in Specair for obtaining the simulation spectra. Alternatively, the slit function can be obtained from a line-shape of an optical emission spectrum at a wavelength close to 360-388nm, which is from the light emitted from a mercury calibration lamp. The best-fit Specair spectrum yields a rotational temperature of 2200 ± 50K. The Specair fit also yields a vibrational temperature of 3400 ± 50K, based on the relative intensities of the (0, 2), (1, 3), (2, 4) and (3, 5) vibrational bands of the N\textsubscript{2} C state.

The quantum efficiency of the spectrometer is wavelength-dependent and this has to be taken into account when interpreting the measured spectra. A calibration curve is therefore needed and this is obtained by comparing the known spectrum of a calibration lamp with the one recorded with the spectrometer. An example of calibration factor curve in 360-385nm is given in Fig 2.10. It is used to calibrate the measured spectra with the Shamrock SR-303i for spectra fitting in Specair to determine the rotational and vibrational temperatures.
2.3.3 Excitation temperature measurement by OES

There are a number of spectroscopic methods for the determination of atmospheric pressure plasma properties. Optical absorption is perhaps the most common of quantitative methods. A beam of collimated light from a visible, ultraviolet, or infrared external source is directed through the plasma and the fraction of light absorbed by specific species is measured. Absolute, line-integrated species densities are determined from this measurement and the knowledge of the absorption coefficient. Laser-induced fluorescence (LIF) is a more sensitive variation of this method that has the advantage of being three-dimensional. However, quantification requires a separate calibration. Both LIF and optical absorption have a disadvantage that they cannot be used to detect many of the more important species present in the plasma that have transitions above 7eV (e.g. O atoms), without either complex vacuum-UV generation or enclosures for the beams, source and spectrometer. In addition to
fluorescence, intense laser beams also scatter light from molecules (Raman scattering\textsuperscript{\textsuperscript{2.21}}) or electrons (Thomson scattering). In Thomson scattering, the wavelength shift of scattered photons with respect to the laser wavelength provides a measurement of electron temperature\textsuperscript{2.22}.

The most widely used optical method for excitation temperature measurement is optical emission spectroscopy\textsuperscript{2.23}. Most of them have been derived from the concept of local thermodynamic equilibrium (LTE), whether full or partial LTE\textsuperscript{2.8, 2.10, 2.24-2.26}. While low temperature atmospheric plasmas are not in equilibrium with their electron, ion and gas temperature being very different from one another, methods based on LTE or pLTE assumptions represent an approximation and a practical diagnosis given the relatively underdeveloped state of the plasma diagnostics for atmospheric discharges. The population and depopulation processes in plasmas are usually in three types of balances: Planck balance, Boltzmann balance and Saha balance with the later two playing a dominant role\textsuperscript{2.24}.

The Boltzmann balance describes the exchange of the internal energy of an atom with the kinetic energy of free electrons in inelastic collisions with the atom. It consists of a forward (excitation) and a corresponding backward reaction (de-excitation)

\[ A_j + e \leftrightarrow \text{B} \rightarrow A_k + e \]  \hspace{1cm} (2.1)

where \( A_j \) and \( A_k \) denote atom \( A \) at its energy level \( j \) and \( k \) respectively. If this balance equilibrates for the two given energy levels and the energy distribution of the free electrons can be assumed to be Maxwellian, the atomic state distribution function (ASDF) obeys the Boltzmann relation\textsuperscript{2.9}.
\[ \frac{\eta_j^B}{\eta_k^B} = \exp \left( \frac{E_j - E_k}{kT_e} \right) \] (2.2)

where \( \eta_j^B = n_j^B / g_j \) is the Boltzmann population density of atom A at its level \( j \), \( n_j \) is the number density of atom A in level \( j \), and \( g_j \) is the statistical weight of level \( j \). \( E_j \) is the excitation energy of atom A at level \( j \) with respect to the ground state, \( k \) is the Boltzmann constant, \( T_e \) is the electron temperature in electron volt.

The production and destruction of the free electrons is governed by the Saha balance:\(^2\)\(^9\)

\[ A_j + e \xrightleftharpoons{} A^+ + e + e \] (2.3)

This links the ASDF to the ionic ground state density \( A^+ \). If this balance equilibrates, the ASDF can be described by the Saha formula:\(^2\)\(^9\)

\[ \eta_j^S = \eta_e \frac{n_e}{2} \left[ \frac{\hbar^2}{2\pi m_e kT_e} \right]^{3/2} \exp \left( \frac{E_j - E_0}{kT_e} \right) \] (2.4)

Here, \( \eta_j^S \) is the Saha population density of atom A at its level \( j \), \( \eta_e \) is the population density of ion \( A^+ \) at the ground state, \( n_e \) is the electron density, \( m_e \) is the mass of electron, \( \hbar \) is the Planck constant, \( E_0 \) is the energy of the ion ground state. Note that two atomic levels which are in the Saha relation with the ionic ground state are interrelated to each other by the Boltzmann relation. When the ASDF applicable to all the energy levels obeys the Saha formula (and also Boltzmann relation), the plasma is said to be in Local Saha Equilibrium (LSE). In this case, the production of free electrons equals the destruction by (three particle) recombination. In other words, the Saha balance is in equilibrium. If only a part of the atomic system (i.e. some energy levels) is populated according to the Saha formula, this part of the atomic system is said to be in partial local Saha
equilibrium \((pLSE)\).\(^2\) These atomic levels which are well described by the Saha relation with the ionic ground state are interrelated to each other by the Boltzmann relation. The excitation temperature determined from the relative or absolute population of these levels equals the electron temperature.

A sketch of the ASDF for LTE plasma and non-LTE ionising plasma (the number of reactions to the right (ionisation) of Eq (2.3) is larger than that to the left (recombination))\(^2\) is shown in Fig 2.11. The horizontal axis is the excitation energy, and the vertical axis is \(\ln \eta_j\). By taking the natural logarithm of Eq (2.4), the following equation can be obtained

\[
\ln \eta_j = \frac{I_j}{kT_e} + \ln \eta_\infty \tag{2.5}
\]

where

\[
I_j = E_e - E_j \tag{2.6}
\]

\[
\eta_\infty = \frac{n_e n_\infty}{2} \left( \frac{\hbar^2}{2\pi m_e kT_e} \right)^{3/2} \tag{2.7}
\]

In a plasma experiment, the atomic population density at one particular energy level can be measured or inferred from optical emission spectroscopy or other optical methods. This is usually done in a plasma volume-averaged and time-averaged fashion, with which the electron density and electron temperature may be assumed as constants for all energy levels (i.e. mean electron energy and mean electron temperature). By the same argument, the ionic population density \(\eta_\infty\) may be assumed as constant as well. Therefore, \(\eta_\infty\) may be considered as constant, and \(\ln \eta_j\) may be plotted as a function of energy levels. This \(\ln \eta_j \sim E_j\) relation should appear as a straight line with a negative slope \(-1/kT_e\), from which \(\eta_\infty\) may be deduced by linear extrapolation according to (2.5). If \(n_e = n_\infty\) (i.e. no multiple ionised particles), the electron density can be
determined from the so-called Saha jump which is the difference between the population density of the highly excited atomic states and the population density of the ionic ground state.\(^2,\!^9\)

![Diagram](image)

Fig 2.11 A sketch of the ASDF for LTE plasma and non-LTE ionising plasma.\(^2,\!^8\) The upper dotted line represents the ASDF in LTE. The solid curve represents a non-LTE ionising plasma. The ratio between the population density of the ground state (level 1) and the first measurably excited state (level 3) gives the temperature \(T_{\text{e}}\), which is smaller than \(T_{\text{e}}\).

For helium plasmas that are discussed in Chapter 5, the helium ions are relatively light and are very easy to diffuse out of the plasmas. New charged particles have to be created continuously to sustain the plasmas. The number of reactions to the right (ionisation) of Eq (2.3) has to be larger than that to the left (recombination), which indicates that helium plasmas discussed in Chapter 5 are ionising plasmas, so the local Saha equilibrium cannot be sustained. This suggests that the actual population density \(\eta_j\) of an excited level \(j\) has to be higher than its Saha equilibrium value \(\eta^*_j\). This can be expressed by an overpopulation factor
\[ b_j = \frac{n_j}{n_j^*} = \frac{n_j / g_j}{n_j^* / g_j} = \frac{n_j}{n_j^*} \] (2.8)

For this ionising plasma, \( b_j > 1 \), that is the atomic states have to be overpopulated. The bigger the value of \( b_j \) is, the larger departure of the plasmas from the LTE state is. The ionisation flow is mainly stepwise in character, a chain of disturbed Boltzmann balances is needed to generate an ionisation flow, which is accompanied by \( b_1 > b_2 > b_3 > ... > 1 \). For each excited level, the number of excitation is more than the number of corresponding de-excitation, \( b_j \) will decrease at higher excited levels\(^{224} \) and so the atomic state distribution at high excitation energy will be close to the LSE. Due to the decreasing \( b_j \) value, the slope of the actual distribution is much steeper than the slope of the Saha distribution, the measured excitation temperature is smaller than the actual electron temperature.

Excitation temperature is calculated by constructing the atomic state distribution function (ASDF) with the absolute density of the ground state and excited helium states (see Chapter 5). The ratio between the population density of the ground state (level 1) and the first measurable excited state (level 3) gives the temperature \( T_{13} \). The slope of the Boltzmann plot of the upper excited energy levels gives \( T_{\text{exc}} \).

### 2.3.4 Electron density measurement by \( H_\beta \) Stark broadening

For plasmas with their electron number density greater than \( \sim 5 \times 10^{13} \) cm\(^3\), the electron number density can be measured from the line-shape of the Balmer \( \beta \) transition (4-2) of atomic hydrogen with the related emission at 486nm (\( H_\beta \) line).\(^{26} \) Although the \( H_\alpha \) line (at 656nm) has higher intensity than \( H_\beta \), it is almost

- 36 -
never used to measure electron density, especially for low electron density, due to its sensitivity for self-absorption and strong broadening by ion dynamics.\textsuperscript{2.30, 2.31}

The above technique requires the addition to the plasma of a small amount of hydrogen (typically 1\% or 2\% mole fraction), which may either come from dissociated water molecules in a humid carrier gas or from premixing H\textsubscript{2} into the gas stream. For detection by emission spectroscopy, the population of atomic hydrogen at electronic state n=4 must be high enough for the H\textsubscript{β} line to be distinguishable from underlying other emission line of plasma. This condition is usually fulfilled in air plasmas with temperature greater than 4000K,\textsuperscript{2.6} or in non-equilibrium plasmas with sufficient excitation of hydrogen electronic states.\textsuperscript{2.6}

The line-shape of the H\textsubscript{β} transition is determined by Lorentzian (Stark, van der Waals, resonance, natural) and Gaussian (Doppler, instrumental) broadening mechanisms that result in a Voigt profile.\textsuperscript{2.32} The total Lorentzian half-width at half-maximum (HWHM) is the sum of the individual Lorentzian HWHMs. The total Gaussian HWHM is the square root of the sum of the squared individual Gaussian HWHMs.\textsuperscript{2.6}

Stark broadening results from interactions of the emitting atoms with the local electric fields of the electrons and ions.\textsuperscript{2.33} Both ions and electrons induce Stark broadening, but electrons make a larger contribution because of their higher relative velocities.\textsuperscript{2.33, 2.34} The Stark broadening width is mostly a function of the electron concentration and a weak function of the gas temperature. Based on a fit of the widths listed by Gigosos and Cardeñoso, the Stark HWHM can be expressed as:\textsuperscript{2.35}

\[
\Delta \lambda_{\text{Stark}} = 1.0 \times 10^{-11} (n_e)^{0.688} \text{nm}
\]  

(2.9)

where \( n_e \) is the electron density in cm\(^{-3} \).
Van der Waals broadening is caused by collisions between excited atoms and neutral perturbers (e.g. N, O, N\textsubscript{2} and O\textsubscript{2} in air plasmas) that do not share a resonant transition with the radiating particle. Its contribution to the Lorentzian HWHM of the H\textsubscript{\beta} line is estimated as:\textsuperscript{2,6}

\[
\Delta\lambda_{vdw} = \alpha / T_g^{0.7} \text{nm}
\]  

(2.10)

As the van der Waals broadening depends on the perturbing molecule, the coefficient $\alpha$ is 1.8 and 2.05 for air and water vapour plasmas, respectively.\textsuperscript{2,6,2.36}

The rotational temperature through the N\textsubscript{2} band is used as an estimate of the gas temperature $T_g$ in unit of K.

If a particle approaching an observer with a relative speed $v$ emits a photon of frequency $\nu_0$ (or wavelength $\lambda_0$) in the reference frame of the particle, the wavelength $\lambda$ of the photon detected by the observer appears shifted from $\lambda_0$ as a consequence of the Doppler effect. The HWHM of the Doppler broadening of the H\textsubscript{\beta} line is given by: \textsuperscript{2,6}

\[
\Delta\lambda_{Doppler} = 1.74 \times 10^{-3} T_g^{0.5} \text{nm}
\]  

(2.11)

It is known that the Stark broadening theory is valid with $n_e \geq 5 \times 10^{13}$ cm\textsuperscript{-3}. If $n_e=5 \times 10^{13}$ cm\textsuperscript{-3}, $T_g= 300$K or 800K, then $\Delta\lambda_{\text{Stark}} = 0.01416$nm. $\Delta\lambda_{vdw} = 0.03690$nm (300K) or 0.01857nm (800K), $\Delta\lambda_{Doppler} = 0.00301$nm (300K) or 0.00492nm (800K). From ref 2.6, in non-equilibrium atmospheric pressure plasmas, $\Delta\lambda_{\text{resonance}} = 0.00200$nm, $\Delta\lambda_{\text{natural}} = 0.00003$nm. The contribution of the resonance and natural broadening to the Lorentzian HWHM is much smaller than the Stark broadening and the van der Waals broadening and thus are neglected. The instrumental broadening is measured using a mercury calibration lamp at 435.8nm. The grating and the entrance slit of the spectrometer (Andor Shamrock) is 2400
groove/mm and 50μm respectively. The instrumental slit function is approximately Gaussian with HWHM of 0.03524±0.00074 nm. Therefore, the HWHMs of Gaussian and Lorentzian broadening are

\[ \Delta \lambda_{\text{Gaussian}} = \sqrt{\Delta \lambda_{\text{Doppler}}^2 + \Delta \lambda_{\text{instrumental}}^2} = 0.03537\text{nm (300K)} \text{ or } 0.03558\text{nm (800K)}, \]

\[ \Delta \lambda_{\text{Lorentzian}} = \Delta \lambda_{\text{Stark}} + \Delta \lambda_{\text{vdw}} = 0.05106\text{nm (300K)} \text{ or } 0.03273\text{nm (800K)}. \]

The resolution of Andor Shamrock spectrometer is 0.023nm when grating is 2400 groove/mm, and the resolution of USB650 Red Tide spectrometer is ~2.0nm. The resolution of spectrometer should be smaller than the full-width at half-maximums (FWHM) of Gaussian and Lorentzian broadening, so the Andor Shamrock spectrometer is appropriate for electron density measurement by H\(_\beta\) Stark broadening when \( n_e \geq 5 \times 10^{13} \text{ cm}^{-3} \).

The total profile can be calculated as the convolution of the profiles due to all the effects (Stark, Doppler, instrumental and van der Waals broadening) for comparison with the experimental one. \( n_e \) is obtained when a best fit between the calculated and measured profiles is reached.\(^{2.36, 2.37}\) If the total profile is a Voigt profile, the HWHM of the total profile (\( \Delta \lambda_{\text{Total}} \)) can be calculated as: \(^{2.36}\)

\[ \Delta \lambda_{\text{Total}} = \left[ \left( \frac{\Delta \lambda_{\text{Lorentzian}}}{2} \right)^2 + \Delta \lambda_{\text{Gaussian}}^2 \right]^{1/2} + \Delta \lambda_{\text{Lorentzian}} \quad (2.12) \]

It is demonstrated that the values of electron density calculated from this equation are in good agreement with the values obtained from the fitting of the experimental and calculated full profiles.\(^{2.36}\)

### 2.4 Fluorescence spectroscopy

Fluorescence spectroscopy employs a beam of light to excite the electrons in molecules of certain compounds and causes them to emit light when transiting to
a lower energy. It is widely used in biochemical, medical and chemical research field for analysing organic compounds. In this thesis, a BMG Labtech Omega micro-plate reader is used to measure hydrogen peroxide concentration in saline solution using Amplex Red Hydrogen Peroxide/Peroxidase Assay Kit (Invitrogen, A22188). This micro-plate reader offers ultra fast UV/Vis absorbance, fluorescence and luminescence (flash and glow). The kinetic fluorescence function with reading data from the top of micro-plates is used to detect the red-fluorescent chemical, resorufin, which is the product of hydrogen peroxide and Amplex Red reagent reaction in the presence of peroxidase. Resorufin has excitation and emission maxima of approximately 571nm and 585nm respectively. So the filter for excitation is in the range of 530-560nm and the filter for emission is at ~590nm.

Fig 2.12 BMG Labtech FLUOstar Omega micro-plate reader.

The definition of instrument parameters and test protocols are realised with the control part of the FLUOstar Omega software. The associated MARS data analysis software package provides several options to display data in a clear and concise format. The linear regression fit is used to generate the standard curve of hydrogen peroxide concentration.
2.5 Ozone detection

Ozone concentration is measured with a chemical method using Gastec ozone detection tubes (Fig 2.13 (a) and (b)). They are thin glass tubes with calibration scales printed on them which allow direct reading of ozone concentrations. Each tube contains detecting reagents that are especially sensitive to ozone and quickly produces a distinct layer colour change. The tubes are hermetically sealed. They need to work with a Gastec detector tube pump (Fig 2.13 (c)) at a proper number of strokes according to the measuring range.

![Gastec ozone detection tubes](image)

Fig 2.13 Gastec ozone detection tubes: (a) # 18M 4-400ppm and (b) # 18L 0.025-3ppm, and (c) Gastec detector tube pump.
Chapter 2 Diagnostics methodology

References


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Chapter 3
AC excited plasmas in contact with liquid

3.1 Introduction

Dynamic interaction of ionised gases with liquid has been an active research area because of the considerable scope and depth of its underpinning science, examples of which include sonoluminescence and co-existence of phases (e.g. gas, liquid, solid and ionised gas). Its impact on practical applications is equally significant including electrolysis, water sterilization, organic contaminant degradation, chemical analysis, material synthesis, microorganism inactivation, surgery, and cancer therapy. There are normally two major types of liquid-containing plasmas, namely above-liquid plasmas and in-liquid plasmas, the former being generated in a relatively stationary gas environment above the gas-liquid interface and the latter being generated in gas bubbles within a liquid medium. They can be generated with different power supply sources including DC, pulse at low repetitive frequency (<hundreds hertz), AC at low frequencies (<hundred hertz), AC at medium frequencies (kilohertz), radio-frequency (RF), and microwave.
DC-excited liquid plasmas are at present the most commonly studied liquid-containing plasmas because they are relatively cheap and easy to realise. Most DC-excited liquid-containing plasmas are above-liquid plasmas generated in air, and they are often used for water treatment and organic contaminants degradation. Electrical and optical characteristics are widely used for their characterisation. Physical properties such as gas temperatures and electron density are obtained in some investigations.\textsuperscript{3.14-3.21}

Pulsed liquid-containing plasmas\textsuperscript{3.22-3.27} are usually used for water purification at frequencies lower than 200 Hz. Current studies in this area are often with a focus on applications with only a few investigations looking into the electrical and optical characteristics of the pulsed liquid-containing plasma.\textsuperscript{3.23,3.25,3.26}

Low-frequency AC-excited plasmas (<300Hz) are well investigated in both theory and applications. Laroussi et al\textsuperscript{3.28-3.30} employed 60Hz power supply to generate non-thermal atmospheric air plasmas with plane-water electrodes (a plane electrode to water configuration). Electrical and optical diagnostics were performed. The discharge behaviours of AC driven plasmas (20-300Hz) with plane-water electrode configuration were studied by Inculet et al.\textsuperscript{3.31-3.33} Characteristics of an AC capillary discharge at 50 Hz and its application were researched by Leys et al.\textsuperscript{3.34-3.38} Locke et al\textsuperscript{3.39, 3.40} reported the influence of AC-excited gliding arc discharges on the property of water and their application for organic dye removal.

At medium frequencies of 1-100 kHz, studies of liquid-containing plasmas are relatively few. Of particular note is a series of studies by ArthroCare on plasmas generated with 100 kHz square wave pulses in water and saline
Chapter 3 AC excited plasmas in contact with liquid

solutions, for which a detailed characterisation of their optical emission spectrum, time traces of voltage and current, and chemical kinetics is reported.\textsuperscript{3.11,3.41-3.43}

For RF excited liquid-containing plasmas, most studies employ excitations at 13.56 MHz\textsuperscript{3.44-3.53} and 27.12 MHz.\textsuperscript{3.54} Microwave liquid-containing plasmas are usually excited at 2.54 GHz.\textsuperscript{3.55-3.59} Their generation is usually made at reduced gas pressure (typically 100-5000 Pa),\textsuperscript{3.55-3.59} though it can also be achieved at atmospheric pressure.\textsuperscript{3.55} Excellent progress in their understanding has been made, for example electron and gas temperature measurement in radio-frequency in-liquid plasmas by Nomura and colleagues\textsuperscript{3.2,3.54-3.60} and detailed emission spectroscopy in microwave in-liquid plasmas by Machala and colleagues.\textsuperscript{3.61}

For DC gas-phase plasmas sustained between two metallic electrodes, each electrode can only act as either the cathode or the anode. Once the applied voltage is below the discharge sustaining value, a DC-excited plasma becomes extinguished immediately because most electrons and ions are lost and there are no sufficient space charges left in the gap to maintain the discharge. For a low-frequency pulse and/or AC discharge, the drop of the applied voltage below the plasma-sustaining voltage causes the discharge to be extinguished as well. Because of their low excitation frequency, discharge events in each half cycle of the applied voltage are often independent from each other and the discharge plasma behaves similar to the case as a positive DC and a negative DC in alternation. One important difference is that the residual time of charges in the electrode gap is longer in the case of an AC discharge, because its usually lower breakdown voltage and the alternative voltage polarity reduce the electron loss to the electrodes. This leads to better energy efficiency of electrical energy
consumption. When the frequency of the applied voltage is above a critical value (usually around tens of kilohertz), the positive ions and/or electrons may remain in the electrode gap because they cannot reach the electrodes before the change of the voltage polarity. The space charges remaining in the gap can facilitate the regeneration of plasmas in the next cycle, or help sustain the discharge at lower electric field. In such cases, discharges during each half cycle become interdependent with each other.

For the reasons discussed above, AC-excited plasmas should be more advantageous than their DC counterparts and this has been demonstrated in the gas phase (i.e. without liquid). It is therefore of interest to examine the validity of this general conclusion for liquid-containing plasmas. DC-excited plasmas in contact with liquid have been well investigated, but studies of AC-excited liquid-containing plasmas have been comparatively few. In the low frequency (<300Hz) range, the difference between DC and AC excited plasmas may not be significant because discharge events in the low frequency AC case may be independent of each other. To explore their possible difference, a higher excitation frequency of 20 kHz is considered in this study of AC-excited liquid-containing plasmas. It will be shown that residual charges start to play an important role in influencing future discharge at this frequency.

### 3.2 Experimental setup

The schematic of the experimental setup is shown in Fig 3.1. The needle electrode is a stainless steel rod with diameter of 5mm. The counter water electrode is a stainless steel plate immersed in 50ml tap water in a plastic container. The distance between the needle tip and the water surface is 2.5mm,
which is adjusted by a micrometer. A 20 kHz power supply is connected to the electrodes. This power supply is built with a function generator (Tektronix AFG 3102), a power amplifier (Amplifier Research, Model 500A100A, 500 watts, 10kHz-100MHz) and a transformer (FLYPVM400, Information Unlimited). The output of the transformer is directly connected to the electrodes. A Tektronix oscilloscope is used to record the voltage and current values. A Tektronix P6015A wideband high voltage probe and a Pearson current monitor are used for the measurements of the applied voltage on the electrodes \( v(t) \) and the discharge current through the electrodes \( i(t) \). Andor iStar ICCD camera is used to take nanosecond images of plasmas.

![Schematic experimental setup](image)

**Fig 3.1 Schematic experimental setup.**

### 3.3 Electrical characteristics

The evolution of the dissipated power \( ( P = \int_0^T v(t)i(t)dt ) \) with the applied voltage is shown in Fig 3.2 while increasing the input power. It is shown that with increasing input power the peak-to-peak value of the applied voltage decreases, but the dissipated power in the plasmas increases. There appears to be two
working modes of the plasmas, of which the temporal properties of the discharge current (see Fig 3.4 and Fig 3.5) suggest a pulsed mode at low input power and a continuous mode at high input power. In the pulsed mode, the applied voltage experiences a large drop of 2.8 kV when the dissipated power increases slowly from 10 W to 18 W. In the continuous mode, the applied voltage only decreases by 0.45 kV but the dissipated power increases by 23 W from 19 W to 42 W.

![Graph](image)

**Fig 3.2** Evolution of the dissipated power with the applied voltage with increasing input power (as indicated by the arrow).

The initial breakdown is shown in Fig 3.3, in which the applied voltage is seen to increase in magnitude and the current remains very small before ~80 μs. At t=80 μs, the gas gap between the needle and the water breaks down at ~17.6 kV, and the current experiences a considerable jump to ~1.5 A. After 80 μs, the applied voltage acquired a non-sinusoidal waveform of much reduced magnitude of ~2.5 kV, but still repeated at 20 kHz. The voltage waveform has a sharp peak during each half cycle, and the voltage peak coincides with a sharp current peak having a variable magnitude between 125-300 mA.
The voltage and current waveforms in the pulsed and continuous modes are shown in Fig 3.4 and Fig 3.5, respectively, both with increasing input power. In Fig 3.4 and at any given input power, the voltage appears to rise to a maximum then drop rapidly accompanied with a sharp current pulse. The drop in the voltage is because the gap becomes much more conductive with plasma generation. The current pulse is formed because the capacitive gas gap has been charged to several kV then discharges through the low impedance of the plasma. The voltage and current waveforms after the current spike are of similar shape and the voltage and current pulses occur approximately simultaneously, indicating a resistive plasma. Fig 3.4 also shows that the first voltage peak and the first current spike decrease in magnitude with increasing input power. However, the second voltage peak and the second current spike actually increase with the input power. Such pulsed-like waveforms of the applied voltage and the current suggest a pulsed plasma, and the region of P=10-18W (see Fig 3.2) is therefore referred to as the pulsed mode. In the pulsed mode, a weak
plasma is formed in each cycle after breakdown, and a small number of residual charges remain either in the gas gap or on the liquid surface to help ignite the discharge in the next cycle. An increase in the input power results in more dissipated power (see Fig 3.2), suggesting that more residual charges remain in the electrode structure for the next discharge event. This reduces the breakdown voltage of the gas gap. At a larger input power, the first peak voltage is lower and the first peak current is smaller. However, an increase in the input power leads to an increase in the second peak voltage and the second peak current. Since the dissipated power increases with the input power (see Fig 3.2), the second voltage peak and the second current peak appear to contribute greatly to the dissipated power. The increase in the input power also results in a more intense plasma.
Fig 3.4 Waveforms of (a) the applied voltage, and (b) the current in the pulsed mode with increasing input power $P$ indicated with the arrow (the dissipated power is 14.7 (black), 15.2 (red) and 17.5W (green) respectively).

With further increase in the input power, many more charges are left from previous discharge events so that the gap is more conductive. The plasma becomes more intense and persists for a longer duration. Eventually the plasma lasts for the entire duration of the applied voltage, as shown in Fig 3.5. This is the continuous mode of the liquid-containing plasma. It is clear from Fig 3.5 that with increasing input power, the applied voltage decreases and the discharge current increases. This suggests a progressively more intense plasma with more charges in the current and greater conduction of the gas gap (lower voltage).
Fig 3.5 Waveforms of (a) the applied voltage and (b) the current in the continuous mode with increasing input power (the dissipated power in each case is marked on the graph). The same colour scheme is used in (a) and (b).

The input power dependence of the discharge is very different in the two modes. To this end, we consider further the case of the pulsed mode. Accumulated charges $Q$ and the time-averaged dissipated powers $P$ in $t_1$ and $t_2$ periods (as marked in Fig 3.4) are shown in Fig 3.6, where all physical quantities are normalised to their own maximum values. It is clear that during the period of the first voltage peak (marked as the $t_1$ period in Fig 3.4), the total charge carried by the first current peak decreases with the total dissipated power. This monotonic decreasing dependence on the total dissipated power also holds for the peak voltage, the peak current, and the dissipated power averaged for the $t_1$
period. Furthermore, the duration of the $t_1$ period reduces with the total dissipated power, including a progressively earlier onset of the gas breakdown (see Fig 3.4(a)). By contrast, all these quantities increase monotonically with the total dissipated power in the period of the second peak voltage (marked as the $t_2$ period in Fig 3.4), suggesting an increasingly greater contribution to the discharge plasma. To see the relative values of each physical quantity in the two periods, their ratios are shown in Fig 3.6. The charge carried in the $t_1$ period, is always smaller than in $t_2$ period, and $t_2$ is always longer than $t_1$. The dissipated power in the $t_1$ period, $P_1$, is always larger than $P_2$, suggesting that the first discharge event makes greater contribution to the total dissipated power.
Chapter 3 AC excited plasmas in contact with liquid

Fig 3.6 Evolution of normalised charges, dissipated power, voltage and current peak in (a) the $t_1$ period and (b) the $t_2$ period, and (c) their ratios with the total dissipated power in the pulsed mode.

3.4 Optical characteristics

Time-resolved nanosecond images with 2ns exposure time in the pulsed mode and the corresponding voltage and current waveforms are shown in Fig 3.7. It is clear that the plasma disappears when the voltage polarity changes.
(points A and I). This is consistent with the occurrence of the voltage and current spikes in Fig 3.4 and confirms the suggestion that the plasma is pulsed with distinct plasma-off phase. The plasma is very intense at the current spike points (C and K). Fig 3.7 suggests that the plasma has different appearances in the positive and negative half cycles. In the positive half cycle, a bright layer of optical emission is seen near the tip of the needle electrode. This is the anode glow. For non-thermal atmospheric pressure plasmas sustained between two parallel plate electrodes, the anode glow (see Fig 1.6) is usually too weak to be visible. In the case of the needle-to-water plasma in Fig 3.7, the electric field at the instantaneous anode (the metal needle) is significantly enhanced by the sharp tip of the needle. Therefore the anode glow is very bright. The bright layer near the water surface is due to the negative glow as the water acts as the cathode in the positive half cycle. In the negative half cycle, the only bright layer is observed near the needle tip. There is no obvious bright layer near the water surface, which is the instantaneous anode, because the flat water surface supports only weak electric field there and so the anode glow is very weak. During the falling edge of the current pulse, the plasma starts to disappear from the middle part of the electrode gap, but remains visible near the electrodes. After the turning point (E and M), the plasma begins to re-develop from the cathode to the anode (G and O). Then they quench again with decreasing current.
A sequence of nanosecond images in the continuous mode are shown in Fig 3.8. These are similar discharge appearances to those in the pulsed mode, for example, the anode glow is visible in the positive half cycle and the negative glow of the cathode fall is very strong in the negative half cycle. The most distinct difference is that the plasma in Fig 3.8 appears to exist in the electrode gap throughout the whole cycle of the applied voltage. This is true even at the polarity transition point (i.e. point A and F). It means that there are always some residual charges left in the electrode gap at 20 kHz. This confirms the suggestion of a continuous mode based on the current waveform of Fig 3.5. These residual charges help sustain the discharge. This allows the electrical power to be used efficiently.
Fig 3.8 Time-resolved nanosecond images in the continuous mode with a dissipated power of 22.2W. The exposure time is 2ns.

The maximum optical intensity and the space-averaged optical intensity are estimated from the nanosecond images in Fig 3.7 and Fig 3.8, and shown in Fig 3.9 as a function of time for the pulsed and continuous modes. It is shown that the optical intensity has the similar time-dependence to the discharge current. In the pulsed mode, plasma emission intensity is very strong during the current pulse and this strong optical intensity is stronger in the positive half cycle. In the negative half cycle, the maximum emission intensity after the current spike is stronger than in the positive half cycle. In the continuous mode, it is shown that the optical intensity in the negative half cycle is much stronger than that in the positive half cycle, indicating that more electrons and active species may be produced in the negative half cycle. In the positive half cycle, the maximum and averaged emission intensities have the similar dynamic profile. But in the
negative half cycle, during the first 5μs period, they do not match well with each other.

Fig 3.9 Space-averaged and maximum optical intensity as a function of time in (a) the pulsed mode and (b) the continuous mode. Plasma conditions are identical to those of Fig 3.7 and Fig 3.8 respectively. The maximum intensity in (a) is shifted upward by 2.

3.5 Effects of plasma on water property

After the plasma treatment, several important properties of water such as pH, conductivity and temperature are often changed due to the chemical reactions between the plasma and the water. The evolution of these properties with
plasma treatment time at different dissipated powers is shown in Fig 3.10. In the pulsed mode (at 14.8, 15.2 and 17.1W in Fig 3.10), pH, conductivity and water temperature change only modestly within the first 25 minutes. However, in the continuous mode (at 22.9W, 28.1W and 36.7W in Fig 3.10), the plasma affects water properties significantly. At 36.7W, the pH value decreases from 7.9 to 3, the conductivity increases from 591µS/cm to 1830µS/cm, and the water temperature increases from 17°C to 62°C after 25 minutes of plasma treatment. It is shown that there are stronger chemical reactions in the continuous mode than those in the pulsed mode.
Fig 3.10 Effects of the plasma on (a) the pH value, (b) the conductivity and (c) the temperature of water in the pulsed mode (open symbols) and the continuous mode (solid symbols). Colour schemes are the same for all three graphs.
The increase of the conductivity is likely to be mainly due to the electrolysis.

The rise of the water temperature is attributed to the heat released from the plasma and conduction through the water. The decrease of pH value is due to the following reactions between active species and water:\(^{3.62}\)

\[
N_2(g) + e \rightarrow 2N + e \quad (3.4)
\]
\[
O_2(g) + e \rightarrow 2O + e \quad (3.5)
\]
\[
N + O \rightarrow NO(g) \quad (3.6)
\]
\[
NO(g) + O \rightarrow NO_2(g) \quad (3.7)
\]
\[
3NO_2(g) + H_2O(l) \rightarrow 2H^+ + 2NO_3^- + NO \quad (3.8)
\]
\[
2NO_2(g) \rightarrow N_2O_4(g) + H_2O(l) \rightarrow HNO_3(l) + HNO_2(l) \quad (3.9)
\]
\[
NO_2(g) + NO(g) \rightarrow N_2O_3(g) + H_2O(l) \rightarrow 2HNO_2(l) \quad (3.10)
\]
\[
3HNO_2(l) \rightarrow HNO_3 + 2NO(g) + H_2O(l) \quad (3.11)
\]
\[
NO_2(g) + OH \rightarrow HNO_3(l) \quad (3.12)
\]

where (g) and (l) denote the gas and the liquid phase. In the continuous mode, the plasma is very intense and reactions (3.4) to (3.7) take place frequently in the plasma in the air above the water. Abundant NO\(_2\) and NO species are generated in the plasma and then they diffuse into the water. Their reactions with water form HNO\(_3\) which is quickly dissociated in water generating H\(^+\) and causing a significant reduction in the pH value.\(^{3.62}\)

### 3.6 Summary

Electrical and optical characteristics of a 20kHz needle-water plasma are presented in this Chapter. There are two modes of the above-water AC excited
Chapter 3 AC excited plasmas in contact with liquid

plasma: the pulsed and continuous modes. In the pulsed mode, the plasma extinguishes when the voltage polarity changes. As a result, the gas gap requires a high applied voltage to breakdown. There are however residual charges left in the electrode gap following a discharge event, and these charges reduce the breakdown voltage from its initial value when the gas gap is broken down for the very first time (i.e. that at ~ 80μs in Fig 3.3). In the continuous mode, the plasma is more intense and always exists in the discharge gap. Plasmas influence the water property such as the pH value, the conductivity and the water temperature due to the chemical reactions between the plasma and water.
Chapter 3 AC excited plasmas in contact with liquid

References


Chapter 3 AC excited plasmas in contact with liquid


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Chapter 3 AC excited plasmas in contact with liquid


Chapter 3 AC excited plasmas in contact with liquid


Chapter 3 AC excited plasmas in contact with liquid


- 73 -
Chapter 4
Contrasting behaviours of liquid-containing AC and DC plasmas

4.1 Introduction

Characteristics of AC excited plasmas in contact with liquids are investigated in Chapter 3. This Chapter presents a comparative study of AC and DC excited plasmas so that their contrast and similarity can be highlighted. It is well known that in the gas phase the physical property (e.g. electron/ion density and temperature) of AC plasmas is more advantageous than those of DC plasmas. In principle, this advantage should also apply to liquid-containing plasmas because a more efficient production of reactive plasma species is likely to result in a more active reaction of these plasma species with liquid. However, plasma properties depend not only on the plasma-forming gas but also on the properties of the liquid that is part of the plasma-containing electric circuit.\(^{4.1,4.2}\) From a practical and economic point of view, both the production of plasma species and their production efficiency need to be considered. Therefore, it is necessary to investigate the difference in energy usage to produce the active species with AC and DC excited plasmas in contact with liquid.

There are two modes in AC excited plasmas: pulsed and continuous modes
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

as described in Chapter 3. These two modes are also present in DC excited

Fig 4.1 Voltage and current waveforms of a DC-excited plasma in contact with a water anode in (a) a self-pulsing mode; (b) the same self-pulsing mode seen over a shorter duration of time; and (c) a continuous mode.
plasmas, depending on the input power, as shown in Fig 4.1. In the self-pulsing mode, the plasma is very weak due to the low input power. There are not enough residual charges (and the electrostatic field thereby produced) to sustain the discharge, so the plasma is generated and quenched aperiodically and it also requires a large voltage to breakdown. In Fig 4.1 (b), the interval between two adjacent pulses varies in 0.75-1.25ms, corresponding to an equivalent frequency of 0.8-1.3kHz. Large current spikes are formed after gas breakdown because the charges accumulated on the gas gap are released through the plasma channel.

In the continuous mode, plasmas are very intense after breakdown because of the high input power. There are abundant charges in the gap to sustain the discharges continuously and therefore the gas breakdown requires only modest voltage. Voltage and current remain constant throughout the experiments for many tens of minutes. The aperiodic character of the self-pulsing mode implies that electrical and indeed any other properties of the DC plasma observed for any given period of time is not necessarily representative of those of plasma in general. Therefore, it is of little value to compare the self-pulsing mode of the DC plasma to the pulsed mode of its AC counterpart. So AC and DC excited plasmas are compared here in their continuous mode.

The experimental setup is the same as in Chapter 3. For DC excited plasmas, a DC power supply (Glassman high voltage INC, PS/MRS, OPO 60-22, 5kV, 60mA) is connected to the electrodes in series with a 25kΩ ballast resistor, a wideband high voltage probe (Tektronix P6015A), a Tektronix P2220 voltage probe and a 10Ω resistor (see Fig 2.1b). An Andor iStar ICCD camera with its associated OES system and the Ocean Optics spectrometer are used to take time-resolved images and optical emission spectrum of plasmas. Two bandpass
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

Filters from Thorlabs (CWL=780nm, FWHM=10nm and CWL=850nm, FWHM=40nm) are used to take images of plasmas for spatially-resolved optical emission intensity of O at 777nm and 845nm.

When recording the full spectrum, a collimating lens is placed in front of an optical fiber to collect all light emission from the plasma and guide it to the spectrometer. The horizontal distance between the lens and the central line of the needle electrode is 4mm.

4.2 Electrical and optical characteristics

4.2.1 Operation range of plasma stability

Electrical characteristics of AC and DC excited plasmas are shown in Fig 4.2. For all the three cases, the applied voltage slightly decreases with increasing discharge current, and the dissipated power increases approximately linearly with increasing current. The voltage of the AC excited plasma is higher than that of the DC excited plasma with water anode but lower than that of the DC excited plasma with water cathode. At any given dissipated power, the DC excited plasma with water anode has the highest discharge current and the lowest plasma-sustaining voltage. In general, the electrical characteristics of the AC excited plasma appear to fall between those of the two DC excited plasmas. The range in the discharge current indicated in Fig 4.2 is that of the continuous mode of DC and AC excited plasmas. The first points of the three curves indicate the lowest discharge current of the plasma to work in the continuous mode. The last points of the three curves are the highest discharge currents that our DC and AC power supply can support.
Fig 4.2 Discharge current dependence of (a) the voltage and (b) the dissipated power for the AC excited plasma and the two DC excited plasmas.

Images of the DC and AC excited plasmas at different dissipated powers are shown in Fig 4.3, with an exposure time of 4ms. It is shown that the diameter of plasma column increases with dissipated power in all three plasmas. There is also an increase in the diameter of the bright layers near the metal and water electrodes. In the case of the DC excited plasma with water cathode, the anode glow near the needle tip is strong and the negative glow near the water surface is visible but less intense. This is due to strong electric field enhancement at tip of
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

the needle electrode. For DC excited plasma with a water anode, the negative
glow near the needle tip (cathode) is intense with a larger diameter than that in
the DC plasma with water cathode in Fig 4.3 (a). There appears a dark region
above the water anode, and this is the anode dark space (see Fig 1.6). The
visible layer near the water surface is indicative of an anode glow but influenced
by the reflection of the cathode glow. The appearance of the AC excited plasma
seems to be the combination of those of the two DC excited plasmas. It is of
interest to note that the width of the near water bright layer changes little with
power, different from the case of Fig 4.3 (b). The schematic diagrams for images
taken at about 28W of dissipated power are shown in Fig 4.4. These are used to
estimate the volume of the plasma. The discharge appearance as shown in Fig
4.4 (b) provides a clear evidence of a glow discharge structure which contains the
negative glow (NG), the Faraday dark space (FDS), the positive column (PC), the
anode dark space (ADS) and the anode glow (AG).

Fig 4.3 Images of (a) the DC excited plasma with water cathode; (b) the DC excited
plasma with water anode; (c) and the AC excited plasma. (All with 4ms exposure time).
Fig 4.4 Images and schematic diagrams of (a) the DC excited plasma with water cathode, (b) the DC excited plasma with water anode and (c) the AC excited plasma at about 28W of dissipated power. (All with 4ms exposure time).

According to the images in Fig 4.3, the discharge volume is estimated and this allows the dissipated power density to be calculated as shown in Fig 4.5. It is clear that the power density does not vary very much with the discharge current for each of the three plasmas. The power density of the AC excited plasma falls between those of the two DC excited plasmas. Given the approximately linear relationship between the dissipated power and the current, this suggests a linear increase of the discharge volume with the dissipated power (see Fig 4.2). Our data match well with the power densities of DC excited plasmas in literature 4.3 and 4.4. The power densities in these prior studies are calculated by using the voltage, current and the plasma volume estimated from the digital images. The difference of ~ 10% between our measurement and those in literatures is excellent, given the assumption of the plasma being circular truncated cone.
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

Fig 4.5 Power density for AC and DC excited plasmas obtained in this work (solid curve) and reported in literatures. (Open symbols: 1-ref 4.3 and 2-ref 4.4. Red is used for DC excited plasma with water cathode, and green is used for DC excited plasma with water anode).

4.2.2 Nanosecond images in the continuous mode

Nanosecond images for the AC excited plasma in its continuous mode have been shown in Chapter 3. Here nanosecond images for the DC excited plasma with water cathode at 20.2W and the DC excited plasma with water anode at 21.0W are shown in Fig 4.6. They are seen to have a similar discharge structure to that of the AC plasma (see Fig 3.8). It is however worth noting that the structure of the DC excited plasmas does not change much with respect to time. Electrons and ions can only move in one direction and finally are lost on the metal and water electrodes (in addition to recombination). In this case, high input power is always needed to generate new electrons and ions. However, in the AC plasma, the alternation of voltage polarity with time helps trap some space charges in the electrode gap and this enable the discharge to be maintained at a low voltage. This reduces the minimum electrical energy necessary to continuously generate
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

electrons and ions.

Fig 4.6 Nanosecond images of (a) a DC excited plasma with water cathode at 20.2W; and (b) a DC excited plasma with water anode at 21.0W. Exposure time is 30ns for the water cathode case and 2ns for the water anode case, respectively, to achieve adequate resolution.

4.3 Gas and water temperatures

As stated in Chapter 2, gas temperature of non-thermal atmospheric plasmas may be approximated by rotational temperature. In low temperature air plasmas, the emission spectrum of the OH (A-X) transition in the range of 306-312nm provides a convenient way to measure the rotational temperature when there is little scope for self-absorption, non-Boltzmann rotational population distribution, and interferences with other species in the plasmas. However, for plasmas in contact with liquid, water vapour results in electronic quenching of OH(A) and this tends to prevent thermalisation of the rotational population distribution of OH (A). This suggests that the OH (A-X) band is unreliable for measurement of rotational temperature of water-containing plasmas. To overcome this, the N₂ band in the range of 360-380nm can be used for measurement of rotational temperature. Here, rotational temperature is measured using both the OH band and the N₂ band for comparison purpose. Rotational temperature with OH band is
obtained by fitting the experimental spectrum with a simulated spectrum obtained using Lifbase. Rotational temperature and vibrational temperature with the N₂ band are obtained by comparison to a simulated spectrum obtained using Specair.

Even without the presence of a liquid medium, the OH band (transition $A^2Σ^+$, $v=0 \rightarrow X^2 \Pi, v'=0$) is frequently observed in atmospheric pressure air plasmas because of moisture in the background air. The rotational temperature can be obtained by fitting the entire OH band, especially for the peaks at 306.5nm, 306.9nm and 309.1nm. Peak at 309.1nm is not sensitive to the change of rotational temperature, and it works as the reference intensity. Peaks at 306.5nm and 306.9nm are quite sensitive to the variation of rotational temperature, and are therefore used for determining rotational temperature.

A rotational temperature obtained from comparing a simulated spectrum with its experimental one is shown in Fig 4.7, for the DC excited plasma with water cathode at a dissipated power of 28.5W. The resolution factor for simulation is 2.1, and the maximum error in rotational temperature is ±100K.

![Rotational temperature obtained with the OH band for a DC excited plasma with water cathode at 28.5W of dissipated power.](image)
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

Rotational temperature measurement using the N$_2$ band (360-380nm) is shown in Fig 4.8 for the DC excited plasma with water cathode at 28.5W. The slit function is obtained by calibration using the emission line-shape at 335nm from a mercury lamp. The FWHM is 0.06729nm after a Voigt fit (see Chapter 2). The rotational and vibrational temperatures are obtained by fitting the experimental spectrum with a simulated one using Specair. Rotational temperature is found to be 2000 ± 50K much lower than the 3000 ± 100K that obtained with the OH band (see Fig 4.7). Vibrational temperature based on the relative intensities of the (0, 2), (1, 3), (2, 4), (3, 5) vibrational bands$^{45}$ of N$_2$ (C) state is 4100 ±50K.

![Rotational and vibrational temperatures obtained using the N$_2$ band for the DC excited plasma with water cathode at 28.5W of dissipated power.](image)

Rotational and vibrational temperatures at different input powers for AC and DC excited plasmas are shown in Fig 4.9. Rotational temperature obtained using the OH band increases with increasing input power for all three plasmas. But rotational and vibrational temperatures obtained using the N$_2$ band remains approximately constant over the range of the dissipated electrical power.
Contrasting behaviours of liquid-containing AC and DC plasmas considered. Rotational temperature obtained using the OH band is much higher than that obtained using the N\textsubscript{2} band. As mentioned above, the OH band is complicated by electronic quenching of OH(A), and so rotational temperature obtained using the N\textsubscript{2} band is more accurate. It is however interesting that measurement using both the N\textsubscript{2} band and the OH band suggest that rotational temperature of the AC excited plasma falls between those of the two DC excited plasmas. This is consistent with the comparison of electrical properties in Fig 4.2 and Fig 4.5.

![Graph](image)

**Fig 4.9** Rotational and vibrational temperatures at different dissipated powers of (a) an AC excited plasma; (b) a DC excited plasma with water anode; and (c) a DC excited plasma with water cathode.

Temperatures of the needle and water electrodes at different input powers after three minutes of plasma treatment are measured using an electronic thermometer and results are shown in Fig 4.10. It is clear that the needle and water temperatures increase with increasing input power in all three plasmas. Again the needle and water temperatures of the AC excited plasma falls between those of the two DC excited plasmas. Interestingly however the needle
temperature of the DC excited plasma is the highest when the needle is the cathode, and the water temperature is the highest when the water is the cathode.

It is known that the electric field is the largest near the cathode surface for glow discharges. This means that the electrons and ions gain their maximum kinetic energy there, and collision of these energetic particles with the background gas result in significant heat generation there.

![Temperature graph](image)

Fig 4.10 Temperatures of the needle and the water after 3mins of plasma treatment.

### 4.4 Production of active plasma species

It is well known that chemically active species like O and OH are capable of degrading organic compounds and inactivating microorganisms.\textsuperscript{4,10,11} It is therefore of great interest to consider the efficiency of production of these species. Emission spectra from 350nm to 900nm by Ocean Optics for all three plasmas are illustrated in Fig 4.11. It is clear that there are many $N_2$ and $N_2^+$ species in the 350-450nm range in addition to N (589nm), H\textsubscript{α} (656nm), N (747nm), O (777nm) and O (845nm) from 550nm to 900nm.
In order to compare the production efficiency of the active species (OH, H\textsubscript{\alpha} and O), relative intensity of OH and absolute intensity of H\textsubscript{\alpha} and O are measured using the Andor OES and Ocean Optics spectrometers at different dissipated powers. OH production efficiency is defined as the relative emission intensity per watt with the emission intensity measured at 309nm (i.e. peak value). At each dissipated power, three measurements are made to indicate statistical variation. Fig 4.12 shows the relationship between the OH production efficiency and the dissipated power. It is seen that the OH production efficiency varies little with the dissipated power. The production efficiency of the AC excited plasma is the largest, being 1.2 times larger than that in the DC excited plasma with water cathode and 1.7 times larger than the DC excited plasma with water anode.
To consider production of other active species, we consider $H\alpha$ and $O$. Normalised absolute intensity spectra at 656nm, 777nm and 845nm at different dissipated powers are plotted in Fig 4.13 using the peak value of the relevant emission. It is clear that the shapes of all the spectra in Fig 4.13 are very similar, and the increment of the peak intensity increases with the dissipated power. This simple relationship is also true for the two DC excited plasmas. It is therefore reasonable to define the $H\alpha$ and $O$ production efficiency as the absolute peak emission intensity per watt of dissipated electrical power.
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

Fig 4.13 Normalised spectra around 656nm, 777nm and 845nm for the AC excited plasma.

The relationship of H\textalpha{} and O production efficiency with dissipated power is presented in Fig 4.14. The H\textalpha{} production efficiency of the AC excited plasma is about 1.75-4 times higher than that of the two DC excited plasmas. H\textalpha{} production efficiency in the DC excited plasma with water cathode is slightly higher than the DC excited plasma with water anode. Similarly the AC excited plasma produces an O emission at 777nm that is about 1.5-2.6 times that of the DC excited plasma with water anode and about 5.6-6.5 times that of the DC excited plasma with water cathode. For atomic oxygen emission at 845nm, its emission intensity per watt in the AC excited plasma is 1.5-2.6 times that of the DC excited plasma with water anode and 5.6-6.5 times that of the DC excited plasma with water cathode. It is clear that the DC excited plasma with water cathode can produce more hydrogen related species and less oxygen species than the DC excited plasma with water anode.

OH and H\textalpha{} species are produced from water vapour dissociation\textsuperscript{4,12,13} and O species are generated mainly from the O\textsubscript{2} dissociation\textsuperscript{4,14,15}. When the water is
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

the cathode, the water temperature is higher than that in the DC excited plasma with water anode, and so the water vapour in the electrode gap is likely to be more thus leading to greater production of OH and Hα. Water vapour can cause two effects on OH and H production: (1) water vapour is the main source to produce OH and H species; (2) water vapour results in the OH and H quenching. Water vapour also has two effects on O species production: (1) larger amount water vapour reduces proportionally the oxygen gas concentration in the gap, thus reduction of O atoms production; (2) water vapour also cause O species quenching. These are the reasons why the DC excited plasma with water cathode has higher production efficiency for OH and Hα and lower production efficiency for O species than that of the DC excited plasma with water anode.

Fig 4.14 Emission intensity per watt at Hα(656nm), O(777nm) and O(845nm) lines as a function of dissipated power.

According to the above comparison of the production of selected active species between AC and DC excited plasmas, it is clear that AC excited plasma
can produce 1.2~5 times higher active species than DC excited plasma for a given dissipated power. One possible reason for this is that AC excited plasmas are time dependent and their in-gap electric field is low while the applied voltage is low. As a result, more charged particles can remain in the gas gap without being lost to the electrodes. Therefore the amount of electrical power required to sustain the plasma is reduced, leading to a better energy efficiency production for reactive plasma species.

Emission intensities considered in the above discussion are spatially averaged. In order to establish regions of the plasma that contain active species, spatially resolved optical intensities of atomic oxygen at 777nm and 845nm are obtained using short-exposed (with 25μs exposure time, equivalent to half period at 20kHz) and wavelength filtered (using bandpass filters) images. Such images are then based to extract the spatial dependence of emission at 777nm and 845nm across the gas from the needle tip to the water surface. The results are shown in Fig 4.15. It is shown that during the positive half cycle of the AC excitation and for the case of water cathode with DC excited plasma, the atomic oxygen intensity at 777nm remains constant along the plasma column except for the position near the water surface (the anode glow region) where the intensity is stronger than those elsewhere. During the AC negative half cycle and for the case of water anode with DC excited plasma, the atomic oxygen intensity near the needle tip is much stronger than that elsewhere. There is a big increase of the oxygen intensity near the needle tip when it is the cathode. The trend for O emission intensity at 845nm is similar. From Fig 4.15, it is clear that the strongest atomic oxygen emission occurs in the cathode region, and this is particularly the case when the needle is the cathode.
4.5 Summary

From the above discussions about the AC and DC liquid-containing plasmas, the following conclusions can be made:

a) AC and DC above-liquid plasmas are glow discharges, within a clear glow structure that contains the negative glow, the Faraday dark space, the positive column, the anode dark space and the anode glow.

b) In the continuous mode, the DC excited plasma is time-independent and requires high power to sustain them.
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

c) Rotational temperature of the AC excited plasma is higher than that of the DC excited plasma with water anode but lower than that of the DC excited plasma with water cathode.

d) $T_{water}$ of the AC excited plasma is lower than that of the DC excited plasma with water cathode and close to that of the DC excited plasma with water anode. $T_{needle}$ of the AC excited plasma is lower than that of the DC excited plasma with water anode, but higher than that of the DC excited plasma with water cathode.

e) AC excited plasma can produce more active species than the DC excited plasma for a given dissipated power.

f) AC excited plasma has the highest energy efficiency among the three liquid-containing plasmas.
Chapter 4 Contrasting behaviours of liquid-containing AC and DC plasmas

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Chapter 5
Characteristics of He/H₂O plasma jets

5.1 Introduction

Stable low-temperature atmospheric plasmas with abundant chemically reactive species (reactive oxygen and nitrogen species) are highly desirable for biomedical applications such as wound disinfection and healing.⁵ ⁷ In particular, reactive oxygen species (e.g. O(^3P), O(^5P), OH⁺, O₂⁻, 'O₂, O, O₃ and H₂O₂⁴ ⁸) are known to be bactericidal. The conventional needle-liquid electrode configuration can be used to generate air or argon-air plasmas and produce with these reactive oxygen species in both the gas phase and the liquid phase.⁵ ⁷ ¹⁰ However, gas and liquid temperatures of such plasmas are usually still too high and this is undesirable to heat-sensitive substrates such as plastics and living tissues.⁵ ¹¹ ¹² High liquid temperature also results in vapour formation near the gas-liquid interface region which makes the plasmas difficult to remain stable and well controlled. Another drawback of the needle-liquid electrode plasmas is that they are not efficient to produce OH and H₂O₂ species due to the limited water vapour content in the plasmas. Hence, it is useful to explore ways to
generate low temperature, stable and reproducible atmospheric plasmas in the presence of abundant water vapour.

At present, there are two methods to increase the water vapour in plasmas: by using a nebuliser to introduce fine liquid droplets into the gas-phase plasma zone\textsuperscript{5.13-5.15} and by electrical discharges within gas bubbles in liquid.\textsuperscript{5.16} For the former case, water vapour is mixed with the after-glow plasma rather than the main plasma in order not to disturb the plasma stability. However this would weaken the ability of the plasma to dissociate H\textsubscript{2}O molecules and produce active H\textsubscript{2}O related reaction chemistry. For the discharges formed in gas bubbles in liquid, the liquid property constantly changes with respect to time during the entire course of the gas discharges. Bubbles which spread and collapse in the liquid are not easy to control, and this makes it difficult to sustain a stable and reproducible plasma.

In order to overcome the above problems, a needle-ring DBD plasma jet with flowing helium gas is considered in this Chapter. Water vapour is introduced by flowing the helium carrier gas through a water container, and this moist helium flow is then mixed with a dry helium flow before the mixed gas is used for gas discharge. Water vapour concentration can be controlled by adjusting the gas flow rate to achieve the required plasma property. This plasma jet can be scaled up by using many such jets in an array for large area plasma treatment.\textsuperscript{5.17}

Characteristic study of the helium/water vapour jet plasmas is performed to better control the plasma condition. Rotational temperature is measured through the N\textsubscript{2} band to establish whether the plasma gas temperature is sufficiently cold not to damage a heat-sensitive substrate. Vibrational temperature through the N\textsubscript{2}
band and excitation temperature through the Boltzmann plot of the absolute helium atom intensity are obtained as an indication of the mean electron energy. The influence of the water vapour concentration in the gas mixture on the active species production is investigated through absolute and relative intensities of nitrogen, oxygen and hydrogen related species. The production mechanisms of these active species are analysed to establish the main parameters that affect production of plasma species.

5.2 Experimental setup

![Schematic experimental setup](image)

Fig 5.1 Schematic experimental setup.

The schematic diagram of the experimental apparatus is shown in Fig 5.1. The powered electrode is a capillary needle with inner and outer diameter of 0.8 mm and 1.2 mm, and a copper ring electrode and a stainless steel plate
electrode are connected to the ground. The frequency of the applied voltage is 20 kHz. The outer and inner diameters of the glass tube are 2 mm and 1.3 mm respectively. The axial distances between different electrodes are indicated in Fig 5.1. The working gas is a helium and water vapour mixture which is obtained by mixing two channels of helium flow, one being a dry helium (99.996%) and the other being dry helium flowing through a water bubbling system. The total gas flow rate is 4slm, and the water vapor concentration is controlled by adjusting the ratio of the dry ($F_{dry}$) and moist helium ($F_{moist}$) flow rates. The optical emission spectrum is measured at the plasma contact point on the surface of stainless steel plate. Ozone concentration is detected through an ozone detection tube (Gastec detection tube) as discussed in Chapter 2.

5.3 Electrical characteristics

The dependence of the dissipated electrical power with the peak-to-peak applied voltage ($V_{pp}$) is shown in Fig 5.2 at different moist helium flow rates. It is evident that there are four different modes with increasing applied voltage, and results shown in Fig 5.3-Fig 5.6 suggest that they are a chaotic mode, a bullet mode, a low current arc mode and a high current arc mode. This is similar to those described in ref 5.18. There is a second chaotic between the bullet mode and the arc mode. In the bullet mode, the dissipated power gradually increases with increasing applied voltage. In the low current arc mode, the dissipated power increases steeply with the increment of the applied voltage. However, in the high current arc mode, the increase in the dissipated power is related to a slight decrease in $V_{pp}$. It is interesting to note that all four modes exist when the moist helium flow rate is lower than 80sccm. The chaotic mode and the low
current arc mode no longer exist when $F_{\text{moist}}$ is higher than 80sccm. The range of the bullet mode becomes shorter with increasing rate of moist helium flow and eventually it disappears when $F_{\text{moist}}$ is higher than 300sccm. The second chaotic mode, however, is always present, and its range becomes larger with increasing rate of the moist helium flow.

![Graph showing dependence of dissipated power on applied voltage at different moist helium flow rates](image)

Fig 5.2 Dependence of the dissipated power on the applied voltage at different moist helium flow rates (0-400sccm). A-the chaotic mode; B-the bullet mode; C-the second chaotic mode; D-the low current arc mode; E-the high current arc mode.

Representative voltage and current waveforms in each mode are shown in Fig 5.3. In the chaotic mode, the discharge currents are not periodic and with accompanying noises. Further analysis using phase portrait and Lyapunkov exponent is outside the scope of this thesis, but is believed to yield confirmation as in the case in a normal dry helium plasma jet. In the bullet mode, the conducting current through the stainless steel plate only appears in the positive half cycle, but it occurs in both positive and negative half cycles in the low
current arc mode. In the high current arc mode, the conducting current through the stainless steel plate is much higher than that in any of the other modes and therefore it causes a distortion in the voltage waveform. Fig 5.3 (c) is the voltage and current waveforms which is close to the bullet mode, and Fig 5.3(d) shows the waveforms near to the low current arc mode. Both figures indicate that waveforms in the transition period are chaotic.

Fig 5.3 Representative voltage and current waveforms: (a) the chaotic mode; (b) the bullet mode; (c) (d) the second chaotic mode; (e) the low current arc mode; (f) the high current arc mode.
5.4 Nanosecond images in the bullet and arc modes

In order to establish the dynamic evolution of the plasma in the bullet and arc modes, nanosecond images are taken at different moist helium flow rates. The exposure time is 10ns. According to the electrical characteristic in Fig 5.2, the plasma only in the bullet and high current arc modes can survive in the large moist helium flow rate range, so nanosecond images in these two modes are investigated here. The chaotic mode is, by definition, not reproducible and so its imaging is not attempted. Voltage and current waveforms for nanosecond images are illustrated in Fig 5.4, with the nanosecond images in the bullet mode and the high current arc mode shown in Fig 5.5 and Fig 5.6 respectively. According to the current waveform in the bullet mode, the magnitude of the current passing through the stainless steel plate decreases significantly with increasing moist helium flow rate, but the value of the current conducting through the ring electrode changes little. Therefore it is valuable to compare the evolution of the plasma plume at different moist helium flow rates in the bullet mode. In the high current arc mode, the increase of the moist helium flow rate does not significantly influence the magnitude of the current passing through the stainless steel plate, there is no significant difference of the evolution of the plasma plume at different moist helium flow rates, so only a representative group of the plasma dynamic evolution images at $F_{\text{moist}} = 0\text{sccm}$ is shown here.
Fig 5.4 Voltage and current waveforms in (a)–(c) the bullet mode with the $F_{\text{moist}}$ at 0sccm, 60sccm and 300sccm; and in (d) the high current arc mode at $F_{\text{moist}}=0$ sccm.

Fig 5.5 shows the nanosecond images of the plasma plume in the bullet mode under the conditions of Fig 5.4a-Fig 5.4c. The instants marked in A, B … K in Fig 5.5 correspond to the same labelled points in Fig 5.4. For each of the three cases in Fig 5.5, a bullet-like image leaves the nozzle exit at instant B and arrives at the ground plate electrode at instant C. As shown in Fig 5.4, the period from B to C corresponds to the rising edge of the current passing through the ground plate electrode. The higher the moist helium flow rate, the less steep the current rising edge and the longer the B-C period time (0.6μs at 0sccm and 1.6μs at 300sccm moist helium flow rate). It is also noted that the volume and optical intensity of the bullet decreases significantly with increasing moist helium flow rate. This can be explained by Lu and Laroussi’s photo-ionisation based model.\textsuperscript{5.19-5.21} In their model, the head of a cathode-directed streamer is a sphere.
containing certain amount of positive ions. As the streamer head moves forward, it leaves behind a quasi-neutral ionised channel with a negligibly low conductivity. The streamer head is not connected to the anode and only the streamer head is measurably luminous. This corresponds to the nanosecond images in the bullet mode. Because of emission of photons from the streamer, photoelectrons are created at a suitable distance from the centre of the sphere. Under the influence of the electric field set up by the space charge, the electrons are accelerated towards the sphere and an avalanche is initiated. If the multiplication up to the sphere is sufficient, the electrons neutralise the positive charge, but leave behind a new positive region. Photons emitted from this region create photoelectrons at a new suitable distance and the process goes on until the bullet arrives at the stainless steel plate. Since there is water vapour in the gas mixture and the plasma bullet travels in the air, electron attachment by water and oxygen molecules plays a key role. The Townsend first ionisation coefficient must be larger than the attachment coefficient, therefore, when this is the case, the electron avalanche initiated by photo-ionisation leads to the plasma bullet formation and propagation. High moist helium flow rate results in the increased electron loss through electron-attachment of water molecules. Hence, the bullet velocity, volume and intensity all decrease with increasing the moist helium flow rate, and eventually the bullet cannot form when $F_{\text{moist}}$ becomes higher than 300sccm, in which the ionisation process is weaker than the attachment process. During the negative half cycle of the applied voltage, there is no bullet formation process, and the plasma is weak between the ring and stainless steel plate electrodes. It is consistent with the low current through the plate electrode observed during this period.
Chapter 5 Characteristics of He/H2O plasma jets

Fig 5.5 Nanosecond images (single shot) in the bullet mode with $F_{\text{moist}}$ being (a) 0sccm; (b) 60sccm; (c) 300sccm moist helium. The ring electrode is in point 1, the tube nozzle exit is in point 2, and the stainless steel plate is in point 3. The exposure time is 10ns.

In the high current arc mode, there are bright plasma plumes in both positive and negative half cycles. In the positive half cycle, the plasma develops from the ring electrode to the stainless steel plate as shown in Fig 5.6. It takes 1.6\,$\mu$s to reach the stainless steel plate when $F_{\text{moist}}$ is 0sccm. In the negative half cycle, the plasma develops from the stainless steel plate towards the ring electrode. The disappearance of the plasma plume happens when the voltage polarity changes, because the current conducting through the stainless steel plate is zero at the polarity reverse point of the applied voltage, space charges left between the ring electrode and the stainless steel plate are not sufficient to help sustain the plasma plume.
5.5 Rotational, vibrational and excitation temperatures

Rotational and vibrational temperatures of the plasma plume of Fig 5.1 in the bullet and high current arc modes at different moist helium flow rates are obtained through optical emission of the N\textsubscript{2} band. They are shown in Fig 5.7 and Fig 5.8 respectively. In the bullet mode, the rotational temperature slightly increases with increasing moist helium flow rate and is not higher than 340K. The vibrational temperature increases first but decreases with increasing moist helium flow rate. Its maximum value is 3550K. In the high current arc mode, the rotational and vibrational temperatures remain constant when $F_{\text{moist}} \leq 120\text{sccm}$. After 120sccm, they increase first then slightly decrease when $F_{\text{moist}} \geq 200\text{sccm}$. The rotational temperature is between 440K and 480K, and the maximum
vibrational temperature is 5300K. Rotational and vibrational temperatures in the high arc mode are both much higher than those in the bullet mode. High vibrational temperature indicates that high energy is stored at the vibrational state of species in the plasma in the high current arc mode, which may help produce more active species than in the bullet mode.

Fig 5.7 Rotational and vibrational temperatures in the bullet mode, at \( V_{p-p} \approx 5 \text{kV} \).

Fig 5.8 Rotational and vibrational temperatures in the high current arc mode, at \( V_{p-p} \approx 5.8 \text{kV} \).
Excitation temperature is calculated by constructing atomic state distribution function (ASDF) with the absolute density of the ground state and four excited helium states which are shown in table 5.1. The elementary occupation of level \( k \) is calculated by:

\[
\eta_k = \frac{4\pi I_{kj}}{A_{kj}E_j D g_k} \quad (5.1)
\]

where \( I_{kj} \) is the transition integrated absolute intensity, \( A_{kj} \) is the spontaneous transition probability, \( E_{jk} = E_k - E_j \) is the difference between the lower and higher atomic energy levels, \( D \) is the depth of the plasma along the line of sight (i.e. the diameter of the plasma plume), \( g_k \) is the statistical weight of level \( k \).

According to the Eq (2.5) and (2.6) in Chapter 2, the natural logarithm of the elementary occupation of level \( k \) is expressed as:

\[
\ln \eta_k = -E_k / kT_e + E_j / kT_e + \ln \eta_e \quad (5.2)
\]

If one plots the relationship between \( \ln \eta_k \) and \( E_k \) for different atomic energy levels, an ASDF can be constructed and the slope of the plot represents \( -1 / kT_e \).

Table 5.1 The transitions in helium used for the determination of the atomic state distribution functions (from NIST\textsuperscript{5,23})

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( E_j ) (eV)</th>
<th>( E_k ) (eV)</th>
<th>( g_k )</th>
<th>( A_{ji} ) ( 10^8 ) s(^{-1} )</th>
<th>Multiplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>447.2</td>
<td>20.964</td>
<td>23.736</td>
<td>7</td>
<td>0.251</td>
<td>( 2^3P^0-4^3D )</td>
</tr>
<tr>
<td>587.6</td>
<td>20.964</td>
<td>23.074</td>
<td>7</td>
<td>0.706</td>
<td>( 2^3P^0-3^3D )</td>
</tr>
<tr>
<td>667.8</td>
<td>21.218</td>
<td>23.074</td>
<td>5</td>
<td>0.638</td>
<td>( 2^1P^0-3^1D )</td>
</tr>
<tr>
<td>706.5</td>
<td>20.964</td>
<td>22.718</td>
<td>3</td>
<td>0.154</td>
<td>( 2^3P^0-3^3S )</td>
</tr>
</tbody>
</table>
If the ground state is labelled by “1”, the first measurable excited state is denoted by “3”. The excitation temperature between these two states $T_{13}$ is obtained through:

$$T_{13} = \frac{E_{13}}{k \ln \left( \frac{\eta_1}{\eta_3} \right)} \quad (5.3)$$

$$\eta_i = n_i / g_i = p / kT_g g_i \quad (5.4)$$

where $p$ is the pressure in Pascal, $T_g$ is the gas temperature of plasmas in Kelvin. The excitation temperature obtained through the Boltzmann plot of the upper excited energy levels is denoted as $T_{\text{exc}}$.

An ASDF in the bullet mode in dry helium (i.e. $F_{\text{moist}} = 0$ sccm) is illustrated in Fig 5.9. As the electron temperature in jet plasmas is typically above 1eV (11605K), it is clearly that the helium jet plasmas are non-equilibrium with both $T_{13}$ and $T_{\text{exc}}$ being smaller than the electron temperature. ASDF in the high current arc mode is similar as in the bullet mode, but the slope of the upper levels (energy higher than 22.718 eV) is less steep than that in the bullet mode. In other words, plasmas in the arc mode are closer to the LTE state.

![Fig 5.9 ASDF in the bullet mode at $F_{\text{moist}} = 0$ sccm for $T_{13}$ and $T_{\text{exc}}$. $E^+$ is the ionisation energy for helium atom, $V_{p-p} = 5$ kV.](image)

Fig 5.9 ASDF in the bullet mode at $F_{\text{moist}} = 0$ sccm for $T_{13}$ and $T_{\text{exc}}$. $E^+$ is the ionisation energy for helium atom, $V_{p-p} = 5$ kV.
Excitation temperatures at $V_{p,p} \approx 5kV$ in the bullet mode and $V_{p,p} \approx 5.8kV$ in the high current arc mode at different moist helium flow rates are shown in Fig 5.10 and Fig 5.11. In the bullet mode, both $T_{13}$ and $T_{exc}$ increase with increasing $F_{moist}$ first, but decrease when $F_{moist} \geq 40sccm$. The maximum value of $T_{13}$ and $T_{exc}$ are 8265K and 3632 ± 809K respectively. When $F_{moist} > 60sccm$, helium emission lines at 447.2nm and 587.6nm are relatively weak in the bullet mode, therefore $T_{exc}$ obtained through the ASDF is not very reliable, and those points are shown in open symbols (see Fig 5.10) to indicate the possible variation trend of $T_{exc}$ at different moist helium flow rates. In the high current arc mode, $T_{13}$ slightly increases with increasing $F_{moist}$ first, but quickly decreases when $F_{moist} \geq 80sccm$. $T_{exc}$ remains constant when $F_{moist} \leq 40sccm$, but increases to the maximum when $F_{moist} = 120sccm$, then decreases with continuously increasing $F_{moist}$. The maximum value of $T_{13}$ and $T_{exc}$ in the high current arc mode are 8937K and 5215 ± 52K respectively. It is indicated that there are more active species in the high current arc mode than that in the bullet mode. The variation of $T_{13}$ and $T_{exc}$ at different moist helium flow rates in both the bullet and the high current arc modes gives an indication that moderate moist helium flow rate is beneficial for the active species production because of the high excitation temperature. However, too much water concentration affects negatively the generation of active plasma species.
Fig 5.10 $T_{13}$ and $T_{exc}$ in the bullet mode, $V_{pp}=5$ kV.

Fig 5.11 $T_{13}$ and $T_{exc}$ in the high current arc mode, $V_{pp}=5.8$ kV.

5.6 Active species and ozone production

Absolute intensity spectra above 350nm obtained with Ocean Optics spectrometer in the bullet and the high current arc modes at the plasma contact point on the ground electrode are shown for $F_{moist}=0$ sccm in Fig 5.12. $V_{pp}$ is about 5kV and 5.8kV in the bullet and high current arc mode respectively. The
major species are nitrogen, oxygen and helium species. The emission intensity of nitrogen and oxygen species is very high because the spectra are measured at the contact point where the ambient air takes part in chemical reactions. It is illustrated that the intensity of active species in the high current arc mode is much higher than that in the bullet mode.

Fig 5.12  Spectra in the bullet and low current arc modes when $F_{\text{moist}} = 0$ sccm, $V_{p-p} \approx 5$ kV in the bullet mode and $V_{p-p} \approx 5.8$ kV in the high current arc mode. (Exposure time is 50μs)

Given that the Ocean Optics spectrometer has a high short-wavelength cut-off at 350nm and its wavelength resolution is only ~2.0nm, an Andor spectrometer with a wavelength range of 180-1100nm and a wavelength resolution <0.2nm is used to measure the relative intensity of some species which cannot be detected by the Ocean Optics spectrometer. The Andor spectrometer is used here to obtain qualitative value of the optical emission as an indication of the concentrations of reactive species. The relative intensity and the wavelength integrated absolute intensity of the active species in the bullet and high current arc modes are shown in Fig 5.13 and Fig 5.14 respectively. In the bullet mode,
optical intensity related to active species increases with increasing $F_{\text{moist}}$ first, but then decrease. The highest intensities of all main species occur when $F_{\text{moist}} = 40\text{scmm}$. The intensities of nitrogen species are much higher than those of the oxygen and hydrogen species. However, as shown in Fig 5.13 (c) and (d), the active species produced by one watt of dissipated power (used as the active species production efficiency) continuously increases with increasing moist helium flow rate. High water vapour concentration does not lead to the high active species concentration (represented by the emission intensity), but results in the high active species production efficiency.

Fig 5.13 Wavelength integrated (a)(c) absolute and (b)(d) relative intensity of the active species in the bullet mode, $V_{pp}=5kV$. 

In the high current arc mode, the intensities of all main species except for OH change slightly when $F_{\text{moist}} \leq 60\text{scmm}$. The emission intensities of nitrogen and oxygen species decrease quickly after the flow rate becomes higher than 60scmm, but the intensity of hydrogen species continuously increases. The
variation of OH intensity with $F_{\text{moist}}$ is totally different from those of other species. It increases fast with increasing moist helium flow rate while $F_{\text{moist}} \leq 120\text{sccm}$, after that it slowly decreases. However, the intensity at $F_{\text{moist}} = 400\text{sccm}$ is still higher than that at 0sccm. The variation of the active species production efficiency with the moist helium flow rate has the similar tendency to that of the actual species concentrations. Although the active species concentration in the high current arc mode (Fig 5.14 (a)) is much higher than that in the bullet mode (Fig 5.13 (a)), the active species production efficiency in the bullet mode (Fig 5.13 (c)) is nearly four times higher than that in the high current arc mode (Fig 5.14 (c)). This is shown that in the bullet mode, the dissipated power in the plasma is used to produce the active species rather than heating the gas (the rotational temperature in the bullet mode is about 100K lower than that in the high current arc mode).

Fig 5.14 Wavelength integrated (a)(c) absolute and (b)(d) relative intensity of the active species in the high current arc mode, $V_{p-p}$=5.8kV.
Ozone production in both the bullet and the high current arc modes at different moist helium flow rates is illustrated in Fig 5.15. It is shown that the ozone production in the high current arc mode is nearly 16 times higher than that in the bullet mode. The ozone production in both modes slightly increases when $F_{moist} \leq 40\text{sccm}$, and decreases quickly when $F_{moist} \geq 60\text{sccm}$,

![Ozone production in the bullet and the high current arc modes at different moist helium flow rates.](image)

**Fig 5.15** Ozone production in the bullet and the high current arc modes at different moist helium flow rates.

### 5.7 Discussion of the active species production mechanism

Results in Fig 5.13-Fig 5.15 show the tendency of how the active species production varies with the moist helium flow rate. In order to understand what factors influence the production of most plasma species, it is useful to discuss possible mechanisms of the active species production in helium/water vapour plasmas. The plasma plume is in contact with the ambient air, so nitrogen and oxygen will in-mix with the helium flow and participate the reactions with helium and water vapour.
Chapter 5 Characteristics of He/H2O plasma jets

In helium-nitrogen plasmas, second positive nitrogen species \( N_2(C - B) \) are normally produced through the electronic excitation and Penning reaction:\(^{5,24}\)

\[
N_2(X) + e \rightleftharpoons N_2(C) + e \quad (5.5)
\]
\[
N_2(X) + He^+ \rightleftharpoons N_2(C) + He \quad (5.6)
\]
\[
N_2(C) \rightarrow N_2(B) + hv \quad (5.7)
\]

The first negative system of nitrogen species \( N_2^-(B^2 \Sigma_u^+ \rightarrow X^2 \Sigma_g^+) \) are produced through the charge transfer and Penning ionisation:\(^{5,25,5,26}\)

\[
He^- + N_2 \rightarrow N_2^+(B^2 \Sigma_u^+) + 2He \quad (5.8)
\]
\[
He^+ + N_2 \rightarrow N_2^+(B^2 \Sigma_u^+) + He + e \quad (5.9)
\]
\[
N_2^+(B^2 \Sigma_u^+) \rightarrow N_2^+(X^2 \Sigma_g^+) + hv \quad (5.10)
\]

\( He^- \) and \( He^+ \) are produced by:

\[
He + e \rightarrow He^+ + 2e \quad (5.11)
\]
\[
He + e \rightarrow He^+ + e \quad (5.12)
\]
\[
He^+ + e \rightarrow He^+ + 2e \quad (5.13)
\]
\[
He^+ + 2He \rightarrow He^- + He \quad (5.14)
\]

The excitation energy of \( N_2(A) \), \( N_2(C) \) and \( He^+ \) is 6.22eV, 11.05eV and 20eV respectively.

In helium-oxygen plasmas, atomic oxygen species \( O(^3P, \varepsilon_{ex} \approx 10.7eV) \) and \( O(^3P, \varepsilon_{ex} \approx 11eV) \),\(^ {5,27,5,30} \) which emit at 777nm \((3p^3P \rightarrow 3s^5S)\) and 845nm \((3p^3P \rightarrow 3s^5S)\) respectively can be generated by electronic dissociation of \( O_2 \) with 6eV and 8.4eV energy to form \( O_2(A^3 \Sigma_u^+) \) and \( O_2(B^3 \Sigma_u^-) \) systems and by collisional excitation with helium metastables, the later plays more important role in the process:
where $O(^1D)$ is the metastable atom.

Ozone is produced by a three body recombination reaction:

$$O + O_2 + M \rightarrow O_3 + M$$ \hspace{1cm} (5.22)

The quenching process of $O(^3P), O(^5P)$ and $O_3$ is as below:

$$O(^3P) + He \rightarrow O + He$$ \hspace{1cm} (5.23)

$$O(^5P) + He \rightarrow O + He$$ \hspace{1cm} (5.24)

$$O(^3P) + O_2 \rightarrow O + O_2$$ \hspace{1cm} (5.25)

$$O(^5P) + O_2 \rightarrow O + O_2$$ \hspace{1cm} (5.26)

$$O + O_3 \rightarrow 2O_2$$ \hspace{1cm} (5.27)

In helium-water plasmas, $O(^3P)$ and $O(^5P)$ can be produced by the electronic dissociation of $H_2O$ with the energy between 17eV and 24eV:

$$e + H_2O \rightarrow O(^3P) + H_2$$ \hspace{1cm} (5.28)

$$e + H_2O \rightarrow O(^3P) + 2H (n = 1)$$ \hspace{1cm} (5.29)

$$e + H_2O \rightarrow O(^5P) + H_2$$ \hspace{1cm} (5.30)

$$e + H_2O \rightarrow O(^5P) + 2H (n = 1)$$ \hspace{1cm} (5.31)

OH (A) and H (n=3)$^{5.31-5.33}$ which emit at 309nm ($OH(A \rightarrow X)$) and 656nm $H_α$ are generated by the direct electronic dissociation of $H_2O/ H_2O^+$ and $He^+_2$:
Chapter 5 Characteristics of He/H2O plasma jets

\[
e + H_2O \rightarrow OH(A) + H (n = 1) \quad (5.32)
\]

\[
e + H_2O \rightarrow OH(A) + H (n = 3) \quad (5.33)
\]

\[
e + H_2O \rightarrow OH + H (n = 3) \quad (5.34)
\]

\[
e + H_2O^+ \rightarrow OH(A) + H (n = 1) \quad (5.35)
\]

\[
He_e^+ + H_2O \rightarrow OH(A) + H^+ + 2He \quad (5.36)
\]

\[
He_e^+ + H_2O \rightarrow OH(A) + HeH^+ + He \quad (5.37)
\]

OH(A), O and H are quenched in H2O as the following reactions:

\[
OH(A) + H_2O \rightarrow OH + H_2O \quad (5.38)
\]

\[
O + H_2O \rightarrow 2OH \quad (5.39)
\]

\[
H + H_2O \rightarrow H_2 + OH \quad (5.40)
\]

OH(A) is also quenched with He as: \( OH(A) + He \rightarrow OH + He \) \( (5.41) \)

From the above reactions, it is evident that the main parameter to influence the active species production is the presence of electrons, either through direct electronic excitation and dissociation, or through reactions with helium metastables and helium ions which are produced by electronic excitation, ionisation and dissociative recombination.\(^{5,34}\) The relationship between these reactions can be illustrated as in Fig 5.16.

Fig 5.16 The pathways to produce reactive species.
Chapter 5 Characteristics of He/H2O plasma jets

Electron density is an important parameter to influence the active species production. Based on the equation (2.7)

$$\eta_e = \frac{n_e \eta_e}{2} \left( \frac{\hbar^2}{2\pi m_e kT_e} \right)^{3/2}$$

and assuming $n_e = n_\infty$, $n_e$ can be estimated by

$$n_e = \sqrt{2 g_e \eta_e} \left( \frac{2\pi m_e kT_e}{\hbar^2} \right)^{3/4}$$

as described in Chapter 2, $n_\infty$ can be obtained by linear extrapolation of the ASDF curve of helium atoms in the bullet and the high current arc mode. As shown in Fig 5.9, note that the high atomic energy level part of the measured ASDF is not in pLTE, so that the slope of the fitted line is too steep and $n_\infty$ is underestimated, which results in a lower electron density than the actual case. $T_e$ should be higher than $T_{13}$ which is derived from the slope in the Boltzmann plot (the maximum value of $T_{13}$ in the bullet and the high current arc modes are 0.71eV and 0.77eV respectively). Since dielectric barrier discharges in an atmospheric pressure helium gap tend to have $T_e$ around 1-4eV, $T_e$ at the contact point on the ground plate electrode is likely lower. $T_e$ is assumed to be 1eV here. The highest $n_e$ value calculated in this way is about $4 \times 10^{12}$ cm$^{-3}$ and $6 \times 10^{13}$ cm$^{-3}$ in the bullet mode and the high current arc mode respectively when $F_{moist}$ is 40sccm. Compared with the electron density range ($10^{11}$–$5 \times 10^{13}$ cm$^{-3}$) estimated for a plasma jet in dry helium and at 1W which has the similar power when $F_{moist}$ is 40sccm in the bullet mode, the above calculated results are reasonable.

The dissipated power calculated from:
Chapter 5 Characteristics of He/H2O plasma jets

\[ P = \int_0^T v(t)(i_{\text{ring}}(t) + i_{\text{metal}}(t))dt \] \hspace{1cm} (5.44)

and the electron density estimated from the current passing through the stainless steel plate in the positive half cycle:

\[ n_e = \frac{\int_0^{T/2} i_{\text{metal}}(t)dt}{e \times V} \] \hspace{1cm} (5.45)

are plotted in Fig 5.17, where \( V \) is the volume of plasma column. Only electrons accumulated in the positive half cycle are considered here because of two reasons: the movement direction of electrons is the same in a half cycle; and

Fig 5.17 (a) Dissipated power and (b) the electron density calculated from current passing through the stainless steel plate in the positive half cycle in the bullet and the high current arc modes.
electrons accumulated in the positive half cycle are dominant in the bullet mode. It is shown that the variation of the electron density with moist helium flow rate has the similar tendency to that of the dissipated power.

The electron density in the bullet mode is not high enough to be detected by H\textsubscript{β} Stark broadening method\textsuperscript{5.38} which requires the electron density higher than $5 \times 10^{13}$ cm$^{-3}$. But the electron density in the high current arc mode can be measured with the H\textsubscript{β} Stark broadening method. The electron density in the high current arc mode measured with the H\textsubscript{β} Stark broadening method\textsuperscript{5.39-5.41} is illustrated in Fig 5.18. The electron density obtained when $F_{moist} > 100$ sccm is not very accurate, because its value is lower than $5 \times 10^{13}$ cm$^{-3}$. The electron density at the plasma contact point with the stainless steel plate increases quickly with increasing moist helium flow rate at first, then decreases sharply when $F_{moist}$ increases from 60sccm to 80sccm. After this point, it decreases slowly with increasing $F_{moist}$. The variation of the electron density at lower moist helium flow rate is more significant than that of the electron density calculated from the current. However the general tendency of the two curves is similar, which means that the electron density conducted from the current can give an indication of the electron density.
According to the calibration curve of H$_2$O concentration in He and helium flow rate through the bubble vessel in ref 5.42, the water concentration is 250-400ppm when $F_{\text{moist}}$ is 40-60sccm which is the transition range for electron density to start to decrease. This is consistent with the data in ref 5.34, where the turning point for the electron density evolution is around 300ppm. At lower moist helium flow rate, the increase of electrons is attributed to the more effective Penning ionisation process. More electrons lead to production of more active species through excitation, dissociation and Penning ionisation. The electron-ion recombination and electron attachment appear to be the main mechanisms responsible for the decrease of electrons with higher moist helium flow rates.

In the bullet mode and when $F_{\text{moist}} \leq 40$sccm, the electron density, the vibrational and the excitation temperatures all increase with increasing moist helium flow rate, so the active species production increases with increasing $F_{\text{moist}}$. When $F_{\text{moist}} \geq 40$sccm, $n_e$, $T_{\text{vib}}$ and $T_{\text{exc}}$ all decrease significantly. At higher moist helium flow rate, more helium metastables become quenched by water.
molecules resulting in less nitrogen, oxygen and OH(A) species being generated through Penning process. More water vapour also results in quenching of these species. Although water vapour is beneficial to generate OH(A) and H(n=3) species, the increment of water vapour contributes little to the net increase of OH(A) and H(n=3) while comparing with the decrease of the n_e, T_vib and T_exc. As a result, all the active species production quickly decreases when the moist helium flow rate becomes higher than 40sccm.

In the high current arc mode and when F_{moist} \leq 40sccm, n_e increases with increasing the moist helium flow rate, T_vib and T_exc remain roughly constant. So the increase of the active species production is attributed to the increment of the electron density. When F_{moist} \geq 40sccm, n_e decreases with increasing moist helium flow rate, but T_vib and T_exc increase. The decrease of the nitrogen and oxygen species production is attributed to the reduction of n_e and the quenching by water molecules. For production of OH(A) and H (n=3) species, the situation is different from the nitrogen and oxygen species. When F_{moist} \leq 120sccm, the production of OH(A) through electronic dissociation of water and helium ions-water reaction is much faster than the quench of OH(A) by water molecules. The increment of T_exc and water vapour plays a more important role than the reduction of n_e in generating OH(A) species. So the OH(A) production increases with increasing moist helium flow rate when F_{moist} \leq 120sccm. But when F_{moist} \geq 120sccm, n_e, T_exc and He_2^+ all decrease and more OH(A) species are quenched by water molecules. So the net production decreases with increasing moist helium flow rate. The variation of H (n=3) production with moist helium flow rate has the similar tendency to that of the vibrational temperature. It is likely that the
energy stored in the vibrational state plays more important role than the electron
density in producing H(n=3) species.

5.8 Summary

Electrical and optical characteristics of the He/H₂O jet plasmas are studied. There are four different modes of the plasma, among which the bullet mode and the high current arc mode are investigated in details. The bullet mode disappears when \( F_{\text{moist}} \geq 300\text{scm} \). Higher moist helium flow rate results in slower bullet velocity and weaker bullet intensity. Production of active species in both the bullet and high current arc modes increases by adding modest amount of water vapour in the gas mixture, but decreases with further increase of water vapour. Rotational, vibrational and excitation temperatures are all influenced by the moist helium flow rate. Electron density, water vapour, excitation and vibrational temperatures play important roles in producing the active species in both the bullet and high current arc modes.
Chapter 5 Characteristics of He/H₂O plasma jets

References


Chapter 5 Characteristics of He/H2O plasma jets


Chapter 5 Characteristics of He/H2O plasma jets


5.23 http://physics.nist.gov/PhysRefData/ASD/lines_form.html. (last access date is on 20 December 2010)


Chapter 5 Characteristics of He/H₂O plasma jets


Chapter 6
Hydrogen peroxide production with different plasma sources

6.1 Introduction

H₂O₂ is one of the most powerful oxidisers with an oxidation potential of 1.8V. It is widely used for organics degradation, drinking water treatment, bacteria killing and wound healing. Plasmas reacting with liquid can generate H₂O₂ accompanied with UV radiation, shock waves, molecular species, ions and reactive radicals which initiate many chemical reactions. Plasmas in or in contact with liquid can be generated by a variety of electrical excitation (e.g. DC, AC or pulse) and using different electrode configurations. Generation rate of hydrogen peroxide is critically influenced by the plasma-liquid interaction. Investigations on the relationship between H₂O₂ production and plasma conditions are important in order to understand how to optimise the H₂O₂ concentration in the liquid. Different H₂O₂ concentrations are appropriate for different applications (e.g. a concentration above 150μM is able to kill E.coli). From an economic point of view, it is also important to identify the appropriate plasma source with the highest energy usage efficiency for hydrogen peroxide production. These are the motivations of this Chapter.
The main pathway for hydrogen peroxide formation is the recombination of hydroxyl radicals through the reaction $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$. Hydroxyl radicals are produced through the electron impact of water: $\text{H}_2\text{O} + e \rightarrow \text{H} + \text{OH} + e$. There are two common methods for measuring hydrogen peroxide concentrations in the solution: iodometric titration and colorimetric method with different reagents (e.g. titanium sulfate, metavanadate, and Amplex red/horseradish peroxidase assay). The colorimetric method with Amplex red/horseradish peroxidase assay and a micro-plate reader is reported in this Chapter due to its easy, accurate and safe procedure.

In this Chapter, we consider hydrogen peroxide production with three plasma sources, namely an AC needle-saline air plasma, a helium/water vapour jet plasma and an argon/water vapour jet plasma, all excited at 20kHz. Saline solution is employed as the treated sample because it is widely used in biological and medical applications. Hydrogen peroxide concentration, the $\text{H}_2\text{O}_2$ production rate and the energy efficiency under different plasma conditions are investigated and compared in detail. The cost of producing one gram of hydrogen peroxide with the three plasma sources is also estimated and discussed.

### 6.2 Experimental setup

The schematics of the experimental setups used in this Chapter are shown in Fig 6.1. The electrode structures are the same as those in Chapter 3 and Chapter 5. The only difference is that the ground electrode is changed to a saline solution (4ml, 0.9% w/v) as the ground electrode. The total flow rate of the dry argon ($F_{\text{dry}}$) and the moist argon ($F_{\text{moist}}$) is 1.8slm, with $F_{\text{moist}}$ being varied from 0 to 90sccm. In the case of helium, $F_{\text{dry}} + F_{\text{moist}} = 4$slm and $F_{\text{moist}}$ is varied from 0 to 200sccm. The
optical emission spectrum is detected at the plasmas-solution contact point using the Andor iStar system. Hydrogen peroxide concentration is determined by using a multimode micro-plate reader (BMG LABTECH FLUOstar Omega) and Amplex Red Hydrogen Peroxide/Peroxidase Assay Kit (Invitrogen, A22188).

Fig 6.1 Schematics of the experimental setups for (a) the He/H₂O or Ar/H₂O jet plasmas; and (b) the needle-saline air plasma.

6.3 H₂O₂ production with AC needle-saline air plasmas

From Chapter 3, it is shown that there are two modes in AC needle-water air plasmas, namely the pulsed mode and the continuous mode. For the AC air plasma with a saline electrode, its voltage and current waveforms are shown in Fig 6.2. They are not dissimilar to those of a corresponding AC air plasma with a water ground electrode in Chapter 3, and this suggests that the AC air plasma with a saline ground electrode is also likely to have the pulsed and the continuous
Chapter 6 \( \text{H}_2\text{O}_2 \) production with different plasma sources

modes.

![Voltage and current waveforms](image)

Fig 6.2 Voltage and current waveforms of an AC needle-saline air plasma in (a) the pulsed mode at 12W of dissipated power; and (b) the continuous mode at 21W of dissipated power. The excitation frequency is 20kHz.

Variation of pH and solution temperature after treatment of the AC needle-saline air plasma is shown in Fig 6.3. The pH value decreases extremely quickly after a short 10s treatment. This reduction is followed by a more gentle decrease with longer treatment time. After 120s of plasma treatment, the pH value is reduced to 3.0 in case of 12W dissipated power and 2.5 with 21W dissipated power. The reduction of pH value is likely due to the production of NO\(_2\) and NO by the plasma and the subsequent production of HNO\(_3\) via their reactions with water.\(^{6,24}\) Solution temperature increases with plasma treatment time. It increases from an initial value of 17°C to 50°C and 68°C, respectively, with 12W and 21W dissipated power respectively after 120s of treatment. It is clear that high dissipated power results in large change in pH value and solution temperature. The time-dependent reduction of the pH value and the solution temperature suggests a possibility of electrical properties (e.g. dissipated power)
Chapter 6 \( \text{H}_2\text{O}_2 \) production with different plasma sources

being a variant, and hence the need for any discussion of \( \text{H}_2\text{O}_2 \) production to account for possible time-dependence. To establish such possibility, dissipated power of the AC plasma is measured as a function of time up to 120s and its maximum variation over this period of time is found to be around 1.9%. Therefore, electrical properties of the AC plasma may be considered to be independent of time.

![Graph showing pH and solution temperature variation with treatment time](image)

**Fig 6.3** Treatment time dependence of (a) pH and (b) the solution temperature with the AC needle-saline air plasma.

Amplex Red assay measures \( \text{H}_2\text{O}_2 \) concentration by means of fluorescence intensity. Its fluorescence intensity varies with the time during which the Amplex
Red assay is in H\textsubscript{2}O\textsubscript{2} solution. Therefore before measurement of H\textsubscript{2}O\textsubscript{2} concentration, it is necessary to establish the incubation time of the sample (Amplex Red assay and H\textsubscript{2}O\textsubscript{2} solution) in the micro-plate reader and obtain the standard curve for the relationship between the fluorescence intensity of Amplex Red assay and the H\textsubscript{2}O\textsubscript{2} concentration. The variation percentage of the fluorescence intensity with the incubation time is shown in Fig 6.4 for different known H\textsubscript{2}O\textsubscript{2} concentrations. It is shown that the fluorescence intensity decreases with the incubation time when the H\textsubscript{2}O\textsubscript{2} concentration is higher than 2.5\textmu{}M, and this trend reverses when the concentration is lower than 2.5\textmu{}M. From Fig 6.4, it is clear that the variation percentage is between -2\% and 5\% when the H\textsubscript{2}O\textsubscript{2} concentration is between 0.625\textmu{}M and 10\textmu{}M. This range is used here as the range with an acceptable accuracy. The standard curve obtained after 30mins of incubation in the micro-plate reader is shown in Fig 6.5, indicating an approximately linear relationship between the fluorescence intensity and the H\textsubscript{2}O\textsubscript{2} concentration when the H\textsubscript{2}O\textsubscript{2} concentration is lower than 5\textmu{}M. For the H\textsubscript{2}O\textsubscript{2} concentration above 10\textmu{}M, they need to be diluted with the buffer solution (sodium phosphate) first before being measured with the micro-plate reader.
Chapter 6 \( \text{H}_2\text{O}_2 \) production with different plasma sources

Fig 6.4 Variation of fluorescence intensity with incubation time.

Fig 6.5 Standard curve for \( \text{H}_2\text{O}_2 \) concentration measurement after 30mins incubation.

Hydrogen peroxide concentration (in \( \mu\text{M} \)), its production rate (in \( \mu\text{M/W} \)) and its production energy efficiency (in g/kWh) are shown as a function of AC plasma treatment time in Fig 6.6. The energy efficiency of \( \text{H}_2\text{O}_2 \) production is defined as

\[
\frac{C_{\text{H}_2\text{O}_2} \times V}{P \times t},
\]

where \( C_{\text{H}_2\text{O}_2} \) is the hydrogen peroxide concentration, \( V \) is the volume of the saline solution, \( t \) is the plasma treatment time, and \( P \) is the dissipated
Chapter 6 $H_2O_2$ production with different plasma sources

electrical power. Since $C_{H_2O_2}$ is in the unit of μM, the above expression need to be converted into the unit of g/kWh by multiplying the molar mass of $H_2O_2$ which is 34.0147g/mol. Fig 6.6 suggests that the AC plasma in the pulsed mode produces more $H_2O_2$ than in the continuous mode. The pulsed mode also has a higher production rate and a greater production energy efficiency. It is of interest to note that $H_2O_2$ production lasts only for a few tens of seconds in both modes, though this finite period of $H_2O_2$ production is longer in the pulsed mode. This may be related to reactions involving iron from the erosion of the needle material (stainless steel), because of its link to Fenton chemistry:\textsuperscript{6.25, 6.26}

\begin{align}
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH^* + OH^- \quad \text{(6.1)} \\
Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + OOHelper^* + H^+ \quad \text{(6.2)}
\end{align}

For other metals such as copper, manganese and cobalt,\textsuperscript{6.26} they also catalyse similar reactions to decompose hydrogen peroxide. These suggest that the presence of metal is usually undesirable for sustained $H_2O_2$ production, because many ionic metals reduce $H_2O_2$ into $OH^*$ radicals and $OH^-$ ions.
Chapter 6 \( \text{H}_2\text{O}_2 \) production with different plasma sources

Fig 6.6 Production of \( \text{H}_2\text{O}_2 \) as a function of plasma treatment time, expressed as (a) \( \text{H}_2\text{O}_2 \) concentration in \( \mu \text{M} \); (b) \( \text{H}_2\text{O}_2 \) production rate in \( \mu \text{M/W} \); and (c) the energy efficiency of \( \text{H}_2\text{O}_2 \) production in g/kWh, all for the case of the AC excited air plasma at two different dissipated powers of 12W (red) and 21W (black). Error bars are due to \( \text{H}_2\text{O}_2 \) concentration measurement, because the variation due to dissipated power is comparably much smaller.
6.4 H₂O₂ production with He/H₂O vapour jet plasmas

The voltage and current waveforms of a helium/water vapour jet plasma employing a saline solution electrode are shown in Fig 6.7. Similar to the He/H₂O plasma with a metallic ground electrode (see Fig 5.3), Fig 6.7 suggests that the bullet mode and the arc mode also exist in the He/H₂O plasma with a saline ground electrode. Fig 6.7 is obtained for the case of $F_{\text{moist}} = 0$ sccm, but the voltage and current waveforms at $F_{\text{moist}} > 0$ sccm are similar to those in Fig 6.7, and so in general the He/H₂O jet plasma with a saline electrode has these two modes. For simplicity, the mode in Fig 6.7 is referred to as the arc mode here without discussing the possible difference between the low-current arc mode and the high-current arc mode as it is the case of Fig 5.3.

![Waveforms of helium/water vapour jet plasma](image)

To confirm the presence of the two modes of the He/H₂O jet plasma, nanosecond images are taken at $F_{\text{moist}} = 100$ sccm and shown in Fig 6.8. It is clear that there are two modes and the nanosecond images in the two modes are
similar to those shown in Fig 5.5 and Fig 5.6.

![Fig 6.8 Voltage and current waveforms and their corresponding nanosecond images in (a), (c) the bullet mode, and (b), (d) the arc mode with $F_{\text{moist}}$ at 100sccm. The ring electrode is in point 1, the tube nozzle exit is in point 2, and the saline solution surface is in point 3. The exposure time is 5ns.](image)

The pH and the solution temperature vary with the plasma treatment time and these are shown in Fig 6.9. In the bullet mode, the pH value does not vary very much with the treatment time for different moist helium flow rates. The solution temperature slightly decreases with the treatment time. The solution temperature under 200sccm of the moist helium flow rate is nearly 3°C lower than that at $F_{\text{moist}} = 0$sccm. In the arc mode, the pH value decreases quickly in the initial 5 minutes, and reaches a steady state afterwards. After 10mins of plasma treatment, the solution temperature increases from 18°C to 37°C at $F_{\text{moist}} = 0$sccm and to 33°C at $F_{\text{moist}} = 200$sccm. Higher moist helium flow rate results in lower solution
Chapter 6 \( \text{H}_2\text{O}_2 \) production with different plasma sources

temperature.

Fig 6.9 Variation of (a) the pH value and (b) solution temperature with treatment time in a helium/water vapour jet plasma, at \( V_{p-p} \approx 4.5 \text{kV} \) in the bullet mode and \( V_{p-p} \approx 6.3 \text{kV} \) in the arc mode. The solid symbol is for the bullet mode and the open symbol is for the arc mode.

Fig 6.10 shows the dependence of \( \text{H}_2\text{O}_2 \) production on the moist helium flow rate at several plasma treatment times. In the bullet mode at \( V_{p-p} \approx 4.5 \text{kV} \), the \( \text{H}_2\text{O}_2 \) concentration decreases first with increasing moist helium flow rate and then increases quickly after \( F_{\text{moist}} \) becomes greater than 40sccm. Longer treatment time results in higher \( \text{H}_2\text{O}_2 \) concentration within 10 minutes of plasma treatment time. However, the increment in \( \text{H}_2\text{O}_2 \) concentration becomes smaller after
10mins. In the arc mode, \( \text{H}_2\text{O}_2 \) concentration is much higher than that in the bullet mode for any given treatment time. Unlike the case of AC air plasma where \( \text{H}_2\text{O}_2 \) production lasts for only a few tens of seconds (see Fig 6.6), the He/\( \text{H}_2\text{O} \) jet plasma is capable of producing \( \text{H}_2\text{O}_2 \) progressively for many minutes and this production appears to increase with time. For the jet plasma, the high voltage needle electrode is insulated with abundant helium and hence little metal is introduced to the plasma. This removes the catalytic reduction of \( \text{H}_2\text{O}_2 \) to  \( \text{OH}^+ \) and  \( \text{OH}^- \) by metal ions in the jet plasma.

Fig 6.10 Variation of \( \text{H}_2\text{O}_2 \) concentration with moist helium flow rate in (a) the bullet mode (at  \( V_{p-p}=4.5\text{kV} \)), and (b) the arc mode (at  \( V_{p-p}=6.3\text{kV} \)).

In order to calculate the production rate of \( \text{H}_2\text{O}_2 \) and its energy efficiency,
dissipated power at different moist helium flow rates in the two plasma modes are shown in Fig 6.11. In the bullet mode, the dissipated power first increase a little with moist helium flow rate and then decreases quickly from 0.49W to 0.05W for the flow rate above 40sccm. In the arc mode, the dissipated power decreases continuously from 7.43W to 6.40W with increasing moist helium rate.

Fig 6.11 Dissipated power in the bullet mode and the arc mode as a function of the moist helium flow rate. These are the averaged values of the dissipated power within 10mins in the bullet mode and 5mins in the arc mode. Error bars are obtained considering two cases with treatment time being 10s and 10mins in the bullet mode, and 10s and 5mins in the arc mode.

The production rate and the energy efficiency are shown in Fig 6.12 as a function of the moist helium flow rate. H₂O₂ production rate and its energy efficiency are seen to increase with the flow rate of the moist helium, mostly probably due to the availability of more water vapour to the electron impact dissociation of H₂O (e + H₂O → H⁺ + OH⁻ + e) and the subsequent production of H₂O₂ via 2OH → H₂O₂ and OH + OH(A) → H₂O₂. This trend is true for F_moist up to 200sccm, which is the 5% of the total helium flow rate and corresponds to approximately 0.12% H₂O concentration in helium, or 1200ppm, according to
measurement data reported recently.\textsuperscript{6,27} Simulation results based on a global model of He + H\textsubscript{2}O plasmas suggest that H\textsubscript{2}O\textsubscript{2} production increases with the H\textsubscript{2}O concentration up to 3000ppm.\textsuperscript{6,28} This is consistent with our experimental results in Fig 6.12.

It is known that the electron impact dissociation of water (\(e+H\textsubscript{2}O \rightarrow H^++OH^-+e\)) requires a threshold electron energy of 5.1eV.\textsuperscript{6,29} Yet large water concentration of up to 1200ppm does not appear to suppress the He + H\textsubscript{2}O plasma and seems to support considerable H\textsubscript{2}O\textsubscript{2} production, indicating the presence of significant amount of electrons with energy above 5.1eV.

Fig 6.12 suggests that the H\textsubscript{2}O\textsubscript{2} production rate is much higher in the bullet mode than in the arc mode, particularly at large flow rates of the moist helium. This is also true for the energy efficiency of H\textsubscript{2}O\textsubscript{2} production. It is however of interest to note that the moist helium flow rate dependence of the energy efficiencies is largely independent of the treatment time in both the bullet and the arc modes, for \(F_{\text{moist}} \leq 200\text{sccm}\) (or H\textsubscript{2}O concentration is about 1200ppm). The time-independence of the energy efficiency is useful for design and operation optimisation when the jet plasma is used as a source of H\textsubscript{2}O\textsubscript{2}. It provides the justification for the plasma to be optimised based largely on the H\textsubscript{2}O concentration. Furthermore, it implies that the characteristics of the jet plasma undergo relatively little variation with time, despite of the rise of solution temperature (see Fig 6.9) and the related possibility of water evaporation.
Chapter 6 \( \text{H}_2\text{O}_2 \) production with different plasma sources

Fig 6.12 \( F_{\text{moist}} \) dependence of the \( \text{H}_2\text{O}_2 \) production rate in (a) the bullet mode \( (V_p \approx 4.5\text{kV}) \) and (b) the arc mode \( (V_p \approx 6.3\text{kV}) \). \( F_{\text{moist}} \) dependence of the energy efficiency is plotted in (c), where the bullet mode and the arc mode are marked with closed and open symbols respectively.

The evolution of the \( \text{H}_2\text{O}_2 \) concentration after one minute of plasma treatment with 120sccm moist helium flow rate in the bullet mode is illustrated in Fig 6.13.
The natural decay of the commercial H$_2$O$_2$ with the similar initial concentration is also shown in Fig 6.13. It is clear that the H$_2$O$_2$ concentration decreases after plasma treatment, and it decreases much quicker after 55 minutes. However, the concentration of the commercial H$_2$O$_2$ nearly keeps constant during the 67mins period. This indicates that there should be some other species in the plasma treated saline solution except for H$_2$O$_2$. Usually, high temperature, UV exposure, transition metal ions, alkalis and strong acids are the main reasons to cause the decomposition of H$_2$O$_2$ to form H$_2$O and O$_2$.\cite{6,30} In this particular case, after plasma treatment, solution temperature is no more than 35°C and the pH value is close to the initial value of 7.5~8. The needle electrode is insulated by helium gas. There should be no transition ions and alkalis in the solution. Therefore high temperature, transition metal ions, alkalis and strong acids cannot be the main reasons to cause the decomposition of H$_2$O$_2$ in our case. UV exposure to the light after plasma treatment is likely to be a reason to cause the H$_2$O$_2$ concentration reduction. However, the plasma generated H$_2$O$_2$ and the commercial H$_2$O$_2$ are kept at the same condition, UV exposure seems not to reduce the concentration of the commercial H$_2$O$_2$, so UV exposure contributes little to the decomposition of the plasma generated H$_2$O$_2$. Therefore, some other reactive species (e.g. O$_2^-$, $^1$O$_2$, OH$^-$) in the plasma treated saline solution may cause the H$_2$O$_2$ decay. It should be emphasised that after switching off the plasma, the H$_2$O$_2$ concentration reduces by a small drop of about 16% over a period of 67mins (or more than one hour). Given that H$_2$O$_2$ is antimicrobial, the results in Fig 6.13 are of great interest as it suggests that liquid after plasma treatment becomes an antimicrobial drug without the need for plasma to be present. The timescale of 1 hour is sufficiently long for systemic delivery. While H$_2$O$_2$ is known to be stable, it would be of
interest to investigate whether there are other plasma-induced reactive species in saline solution (such as \(\text{O}_2^-\)) and whether they could be held at relatively high concentrations for a relatively long period of time. This line of investigation is however outside the scope of this thesis.

![Graph showing gradual decay of \(\text{H}_2\text{O}_2\) concentration after 1 min of plasma jet treatment.](image)

**Fig 6.13** Gradual decay of \(\text{H}_2\text{O}_2\) concentration after 1 min of plasma jet treatment (\(F_{\text{moist}} = 120\text{sccm}\) in the bullet mode). Open symbol represents the concentration of commercial \(\text{H}_2\text{O}_2\), and solid symbol represents the concentration of plasma generated \(\text{H}_2\text{O}_2\) in saline solution.

### 6.5 \(\text{H}_2\text{O}_2\) production with \(\text{Ar}/\text{H}_2\text{O}\) jet plasmas

Before measurement of hydrogen peroxide production in saline solution by an argon/water vapour jet plasma, it is necessary to investigate the characteristics of argon/water vapour jet plasmas to establish the region of stable plasma operation. The voltage and current waveforms of an argon jet plasma with \(F_{\text{dry}} = 1.8\text{slm}\) and \(F_{\text{moist}} = 0\text{sccm}\) are shown in Fig 6.14. The corresponding digital photos are presented on the left of the graph. It is clear that the current waveforms are not periodic when the plasma plume is out of the tube, suggesting that the argon jet plasma is perhaps not as stable as its corresponding helium...
plasma. If the input power is further increased ($V_{p-p} \geq 7.6\text{kV}$), the Ar/H$_2$O jet plasma becomes as a very intense but unstable arc. There is considerable distortion to the voltage waveform and the plasma dynamics are too violent to be useful. In this Chapter, the work on argon jet plasma is confined to the region with the voltage and current waveforms being similar to those in Fig 6.14 (b). This is also the condition under which the plasma plume interacts with the saline solution directly.

![Voltage and current waveforms](image)

Fig 6.14 Voltage and current waveforms of an Ar/H$_2$O jet plasma when the plasma is (a) contained in the quartz tube ($V_{p-p} = 4.5\text{kV}$), and (b) ejected out of the tube nozzle ($V_{p-p} = 6\text{kV}$). ($F_{dry} = 1.8\text{slm}$ and $F_{moist} = 0\text{sccm}$).

The rotational and vibrational temperatures of the argon plasma obtained using the N$_2$ (C-B) band (see Chapter 2 for method) are shown in Fig 6.15. They are measured at different moist argon flow rates at the same applied voltage of $V_{p-p} = 7.2\text{kV}$. The rotational temperature is around 300K and increases slightly with
increasing moist argon flow rate by ~20K. With increasing moist argon flow rate, the vibrational temperature first increases by 150K and then decreases almost linearly at a rate of 7.5K/sccm when \( F_{\text{moist}} \) is higher than 30sccm.

![Diagram](image)

Fig 6.15 Rotational and vibrational temperatures at different moist argon flow rates and with the applied voltage held at \( V_{p-p} \approx 7.2kV \).

In the gas phase, production of active species and ozone at different moist argon flow rates is shown in Fig 6.16 for \( V_{p-p} \approx 7.2kV \). Similar to the technique used in Chapter 3-5, optical emission associated with an active plasma species is used as an indirect indicator of the production of the active species. Ozone measurement is based on a chemical method as discussed in Chapter 2. Of the three argon emission lines considered, optical intensity at 545nm changes very little over the entire range of \( F_{\text{moist}} = 0 \sim 90 \text{sccm} \), whereas that at 826nm also remains approximately constant until \( F_{\text{moist}} = 50 \text{sccm} \) and undergoes a slight decrease above \( F_{\text{moist}} = 50 \text{sccm} \). The strongest argon line at 763nm has an initial phase of gradual increase from \( F_{\text{moist}} = 0 \text{sccm} \) to 50sccm after which it experiences a 3.5 fold reduction in emission intensity. Of active plasma species, three N\textsubscript{2}
emission lines are considered (at 317, 337 and 358nm) and they follow a similar trend of three phases: an initial increase in emission intensity in $F_{\text{moist}}=0$-10sccm, an intermediate phase of a very slight decrease in $F_{\text{moist}}=10$-50sccm, and finally a rapid decrease to $F_{\text{moist}}=90$sccm.

The OH emission at 309nm appears to remain approximately constant, whereas the ozone concentration decreases with increasing $F_{\text{moist}}$ and this reduction is more significant above $F_{\text{moist}}=50$sccm. Atomic oxygen emissions at 777nm and 845nm are too weak to be detected. The trend of the $N_2$ emission lines and the argon line at 763nm is broadly consistent with that of the vibrational temperature in Fig 6.15 through $T_{\text{vib}}$ starts to reduce at a smaller $F_{\text{moist}}$ of 40sccm. At $V_{p-p}=7.2$kV and in the mode of Fig 6.14 (b), the argon plasma is not very intense particularly at large water vapour concentration.

![Fig 6.16 Active species intensity and ozone production at different moist argon flow rates and with the applied voltage held at $V_{p-p}=7.2$kV.](image)

The variation of pH value and solution temperature with the treatment time of the argon/water vapour jet plasma at $V_{p-p}=7.2$kV is shown in Fig 6.17. The pH...
value undergoes a very similar reduction of 3.3 from 7.9 to 4.6 after 10 minutes of plasma treatment for \( F_{\text{moist}}=0 \text{scm} \) and 90scm. This reduction in pH value is smaller than that seen in the arc mode (see Fig 6.9) of the He/H\(_2\)O vapour jet plasma (from 7.7 to 3.8), but larger than that of the He/H\(_2\)O vapour jet plasma in its bullet mode. The reduction of pH value is independent of \( F_{\text{moist}} \) in both the helium jet plasma and the argon jet plasma. After 10mins of the argon plasma treatment, the solution temperature decreases from an initial temperature of 20\(^\circ\)C to 14\(^\circ\)C and to 13\(^\circ\)C at \( F_{\text{moist}}=0 \text{scmm} \) and 90scm respectively. Higher moist argon flow rate appears to result in a lower solution temperature.

![Graph showing pH and solution temperature over time](image)

Fig 6.17 Treatment time dependence of (a) pH, and (b) solution temperature with an Ar/H\(_2\)O vapour jet plasma held at \( V_{pp}=7.2kV \).
Fig 6.18 shows $\text{H}_2\text{O}_2$ concentration, its production rate and the energy efficiency at different moist argon flow rates. The hydrogen peroxide concentration decreases first with increasing $F_{\text{moist}}$ then increases quickly when $F_{\text{moist}}$ is higher than 30sccm. Longer treatment time results in more hydrogen peroxide generation. This trend in $\text{H}_2\text{O}_2$ concentration is similar to that of the He/$\text{H}_2\text{O}$ vapour jet plasmas (see Fig 6.10), and the minimum $\text{H}_2\text{O}_2$ concentration occurs 20-40sccm in both plasmas. In terms of the amount of $\text{H}_2\text{O}_2$ concentration, the Ar/$\text{H}_2\text{O}$ jet plasma in Fig 6.18 (a) compares well with the bullet mode of the He/$\text{H}_2\text{O}$ jet plasma in Fig 6.10 (a) for both plasma treatment times (1min and 10mins). At $F_{\text{moist}} = 90\text{sccm}$, $\text{H}_2\text{O}_2$ concentration after 10mins is about 12.5 times than that after 1min, suggesting that longer treatment time is more efficient. The $\text{H}_2\text{O}_2$ production rate and the energy efficiency vary only slightly with moist argon flow rate. The $\text{H}_2\text{O}_2$ production rate (Fig 6.18 (c)) after 10 minutes treatment is about 13-17 folds of that with 1 minute treatment, whereas the energy efficiency (Fig 6.18 (d)) after 10mins is about 1.5 times than that after 1min. These results suggest that longer treatment time with Ar/$\text{H}_2\text{O}$ jet plasma is likely to lead to better energy efficiency of $\text{H}_2\text{O}_2$ production. It should be noted that the $F_{\text{moist}}$ dependence of both the production rate and the energy efficiency is approximately constant in the Ar/$\text{H}_2\text{O}$ jet plasma, very different from that of the He/$\text{H}_2\text{O}$ plasma (see Fig 6.12). The $\text{H}_2\text{O}_2$ production rate and the energy efficiency are much smaller in the Ar/$\text{H}_2\text{O}$ jet plasma.
Chapter 6 H$_2$O$_2$ production with different plasma sources

Fig 6.18 H$_2$O$_2$ production in the Ar/H$_2$O jet plasma ($V_{p-e}$=7.2kV): (a) H$_2$O$_2$ concentration; (b) dissipated power (averaged value within 10mins); (c) H$_2$O$_2$ production rate; (d) the energy efficiency. Error bars are due to dissipated power variation, because the error due to H$_2$O$_2$ measurement is comparably much smaller.

The evolution of H$_2$O$_2$ concentration after 10 minutes of Ar/H$_2$O jet plasma treatment with $F_{moist}$ =0sccm is shown in Fig 6.19. The natural decay of the commercial H$_2$O$_2$ with the similar initial concentration is also plotted here. H$_2$O$_2$ concentration is seen to decrease slowly of only 6% over the first 40 minutes after switching off plasma, then reduce much quicker to reach an overall reduction of about 22% after 70mins, which is slightly greater than that in the bullet mode of the He/H$_2$O jet plasma (see Fig 6.13). The solution temperature is very low after plasma treatment (see Fig 6.17 (b)), so temperature is not a key reason for H$_2$O$_2$ decomposition. pH value decreases to 4.6 after plasma treatment. The needle electrode is insulated by argon gas and no metal is introduced to the plasma. Therefore transition metal ions, alkalis and strong acid are not the reason for reduced H$_2$O$_2$ concentration. UV exposure seems not to reduce the concentration
of the commercial H$_2$O$_2$, so UV exposure contributes little to the decomposition of the plasma generated H$_2$O$_2$. Therefore, some other reactive species (e.g. O$_2^-$, $^{1}$O$_2$, OH') in the plasma treated saline solution may cause the H$_2$O$_2$ decay.

![Graph showing dynamics of H$_2$O$_2$ concentration after 10mins of argon plasma treatment at $F_{moist} = 0$scm.]

Open symbol represents the concentration of commercial H$_2$O$_2$, and solid symbol represents the concentration of plasma generated H$_2$O$_2$ in saline solution.

### 6.6 Comparison of H$_2$O$_2$ production with different plasmas

In section 6.3-6.5, H$_2$O$_2$ production using three different types of atmospheric plasmas has been discussed in terms of its dependence on plasma conditions, water vapour concentrations in the plasma-forming gas, and treatment time as well as its production rate and energy efficiency. Distinct differences are observed, and these offer a useful knowledge base from which to undertake a detailed mechanistic study by considering some of the fundamental plasma parameters (e.g. vibrational and excitation temperatures, electron density, and rotational temperature) as well as key reactions in the water-containing plasma chemistry. This mechanistic study is however outside the scope of this thesis, as the focus here is to identify one or more appropriate plasma sources for H$_2$O$_2$ production as
well as their operating conditions for applications that can benefit from plasma-mediated ROS chemistry near room temperature.

Although \( \text{H}_2\text{O}_2 \) is available commercially in both liquid and gaseous forms, the benefits of plasma-produced \( \text{H}_2\text{O}_2 \) are that \( \text{H}_2\text{O}_2 \) efforts are enhanced synergistically by other plasma-produced reactive oxygen species in the plasma treated liquid, such as \( ^1\text{O}_2, \text{O}_2^-, \text{O}, \text{OH}^- \) and \( \text{NO} \). In the scenario where an above-liquid plasma provides \( \text{H}_2\text{O}_2 \) as well as other reactive oxygen species through its continuous application to and interaction with the downstream water-containing sample (such as an open wound), their synergistic effects are sustained for the plasma-on duration. For the case where a plasma-treated liquid is used subsequently (i.e. after plasma treatment) as a source of ROS including \( \text{H}_2\text{O}_2 \) for biomedical applications, such liquid is effectively a (plasma-induced) drug due to its biological effects (e.g. antimicrobial and/or anticancer) and this suggests an exciting possibility of plasma pharmacy depends on the lifetime of plasma-induced ROS in the liquid. \( \text{H}_2\text{O}_2 \) has a long half-life and this is shown in Fig 6.13 and Fig 6.19, whereas \( \text{OH}^- \) radicals are known to react with other substances within a few Å of their production location. Recent studies of liquid-containing plasmas suggest that \( \text{O}_2^- \) may maintain a high concentration in liquid several tens of minutes after plasma treatment, suggesting that the long half-lives of \( \text{H}_2\text{O}_2 \) as shown in Fig 6.13 and Fig 6.19 may be extended to other reactive oxygen species such as \( \text{O}_2^- \) and \( ^1\text{O}_2 \). At present, in-liquid measurement of ROS other than \( \text{H}_2\text{O}_2 \) is rare and there is also a clear need for measurement calibration and specificity. Given this, our work here is focused on \( \text{H}_2\text{O}_2 \) as an indicator of how in-liquid ROS are produced efficiently using different plasma sources.
For bio-medical applications, low-temperature treatment is important because of widespread use of thermally labile materials such as plastics and human tissues. The cost of helium and/or argon usage can be considerably mitigated by means of recycling the gas. Electricity cost needs to be considered, however, given that low-temperature plasmas can be and have been used to disinfect hospital wards and the electricity cost of such large plasma system may become a limiting factor.

It is clear that the maximum $\text{H}_2\text{O}_2$ concentration is achieved with the AC air plasma at about 180μM after only 40 seconds of treatment. The sharp reduction of $\text{H}_2\text{O}_2$ concentration after 40s is due to $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ reduction of $\text{H}_2\text{O}_2$ into $\text{OH}^-$ and $\text{OH}^-$ via Fenton’s reaction (see Eq (6.1) and (6.2)). $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ are from the stainless steel needle and formed in the saline solution. Such effects are also expected to take place with the naked needle electrode made from other metals such as copper, zinc, and manganese. If the electrode is insulated or made of metals that cannot decompose $\text{H}_2\text{O}_2$ (e.g. magnesium), such reduction should be at least mitigated. By contrast, the He/$\text{H}_2\text{O}$ jet plasma and its argon counterpart have gas insulated electrode and therefore metal ions are not involved in the underpinning reactions in any significant way, thus removing the $\text{H}_2\text{O}_2$ decomposition pathway via Fenton’s reactions. This explains the monotonic increase of $\text{H}_2\text{O}_2$ concentration with plasma treatment time, as shown in Fig 6.20 (a). Therefore the jet plasmas with insulated electrodes represent a more reliable source of plasma-produced ROS whose concentrations may be controlled simply by plasma-on time.
As discussed in section 6.3, the air plasma has a high gas temperature and consumes significant electrical power. This is reflected in its poor $\text{H}_2\text{O}_2$ production rate that peaks at ~$14\mu\text{M/W}$, a factor of 215 lower than that of the He/$\text{H}_2\text{O}$ jet plasma (~$3000\mu\text{M/W}$) after 10mins of treatment and with $F_{\text{moist}}=200\text{scm}$. In the
case of the Ar/H\textsubscript{2}O jet plasma, the maximum H\textsubscript{2}O\textsubscript{2} production rate is 196\(\mu\text{M/W}\), still higher than the air plasma. This is consistent with the difference in dissipated power between an atmospheric helium plasma and its argon counterpart.\textsuperscript{6,34}

The energy efficiency is also the highest with the He/H\textsubscript{2}O jet plasma, as shown in Fig 6.20 (c). The comparison of the energy efficiency between the two jet plasma is very similar to that of the H\textsubscript{2}O\textsubscript{2} production rate (Fig 6.20 (b)). It is of interest to note that the initial increase of the energy efficiency with respect to time is similar in the He/H\textsubscript{2}O jet plasma and the air plasma, suggesting that the H\textsubscript{2}O\textsubscript{2} production during the first 30s of plasma treatment may be related to similar reactions and electrons of similar density and mean energy. The leveling off in the energy efficiency after 1min in the He/H\textsubscript{2}O jet plasma may indicate a steady state being reached.

The maximum energy efficiency of 2.4g/kWh achieved in the He/H\textsubscript{2}O jet plasma at \(F_{\text{moist}}=200\text{sccm}\), comparing favorably with those reported in literature (Table 6.1). It is third to 7.8g/kWh (achieved with a capillary plasma excited at 50Hz and with Na\textsubscript{2}HPO\textsubscript{4}\textsuperscript{•}2H\textsubscript{2}O as the media\textsuperscript{6,35}) and 3.64g/kWh (achieved with a pulsed streamer corona excited at 60Hz and with Potassium chloride as the liquid\textsuperscript{6,38}). It is possible that the use of Na\textsubscript{2}HPO\textsubscript{4}\textsuperscript{•}2H\textsubscript{2}O and Potassium chloride in our experiments may increase the energy efficiency. It is certainly possible that an increase in \(F_{\text{moist}}\) will increase the energy efficiency.
Chapter 6 $\text{H}_2\text{O}_2$ production with different plasma sources

Table 6.1 Comparison of $\text{H}_2\text{O}_2$ production with other plasma methods

<table>
<thead>
<tr>
<th>Discharge</th>
<th>Power (W)</th>
<th>Liquid</th>
<th>$\text{h}_{\text{H}_2\text{O}_2}$ (g/kW·h)</th>
<th>pH</th>
<th>$T_{\text{water}}$ (°C)</th>
<th>Ref</th>
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</thead>
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<tr>
<td>Capillary</td>
<td>18.3</td>
<td>$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$</td>
<td>7.8</td>
<td>-</td>
<td>80</td>
<td>6.35</td>
</tr>
<tr>
<td>Pulsed in bubble (Ar)</td>
<td>30</td>
<td>Tap water</td>
<td>0.843</td>
<td>-</td>
<td>43-50$^\text{a}$</td>
<td>6.36</td>
</tr>
<tr>
<td>Pulsed streamer corona</td>
<td>140</td>
<td>Phenol/Hydroquinone</td>
<td>0.075</td>
<td>3-3.5</td>
<td>25-30$^\text{a}$</td>
<td>6.37</td>
</tr>
<tr>
<td>Gliding arc</td>
<td>500</td>
<td>Tap water</td>
<td>0.026</td>
<td>4.85</td>
<td>-</td>
<td>6.24</td>
</tr>
<tr>
<td>Pulsed streamer corona</td>
<td>22.8</td>
<td>Potassium chloride</td>
<td>3.64</td>
<td>3.8</td>
<td>20$^\text{a}$</td>
<td>6.38</td>
</tr>
<tr>
<td>DC diaphragm</td>
<td>456</td>
<td>$\text{NaCl}$</td>
<td>0.74</td>
<td>-</td>
<td>15$^\text{a}$</td>
<td>6.39</td>
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<tr>
<td>DC in water</td>
<td>41</td>
<td>$\text{KCl}$</td>
<td>1.52</td>
<td>-</td>
<td>24$^\text{a}$</td>
<td>6.40</td>
</tr>
<tr>
<td>Pulsed</td>
<td>&lt;90</td>
<td>$\text{KCl}$</td>
<td>1</td>
<td>-</td>
<td>20$^\text{a}$</td>
<td>6.12</td>
</tr>
<tr>
<td>Plasma torch (Ar)</td>
<td>2</td>
<td>PBS</td>
<td>$8.925 \times 10^{-5}$</td>
<td>7.4</td>
<td>&lt;30</td>
<td>6.41</td>
</tr>
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<td>Needle-saline</td>
<td>12.2</td>
<td>Saline solution (0.9% w/v NaCl)</td>
<td>0.83</td>
<td>4.1</td>
<td>22</td>
<td>This work</td>
</tr>
<tr>
<td>Needle-ring plasma jet (He/$\text{H}_2\text{O}$)</td>
<td>0.05</td>
<td>Saline solution (0.9% w/v NaCl)</td>
<td>2.46</td>
<td>7.7</td>
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<td>This work</td>
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<td>Needle-ring plasma jet (Ar/$\text{H}_2\text{O}$)</td>
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<td>Saline solution (0.9% w/v NaCl)</td>
<td>0.2</td>
<td>4.6</td>
<td>14</td>
<td>This work</td>
</tr>
</tbody>
</table>

a. With extra cooling system

6.7 Summary

All the three plasma sources are effective in production of $\text{H}_2\text{O}_2$ in saline solution. AC needle-saline air plasmas are not able to sustain $\text{H}_2\text{O}_2$ production for much more than 40s due to decomposition of $\text{H}_2\text{O}_2$ by iron ions via Fenton’s reaction. For He/$\text{H}_2\text{O}$ and Ar/$\text{H}_2\text{O}$ jet plasmas, longer treatment time results in higher $\text{H}_2\text{O}_2$ concentration in the solution. $\text{H}_2\text{O}_2$ production rate with helium jet plasmas is not affected by the duration of plasma treatment, while $\text{H}_2\text{O}_2$ production rate with argon jet plasmas slightly increases with the treatment time. The highest energy efficiency of $\text{H}_2\text{O}_2$ production is achieved with the He/$\text{H}_2\text{O}$ jet plasma at $F_{\text{moist}}=200$ sccm.
Chapter 6 H₂O₂ production with different plasma sources

References


Chapter 6 \( \text{H}_2\text{O}_2 \) production with different plasma sources


6.27 Bruggeman, P., Iza, F., Lauwers, D. and Gonzalvo, Y.A. 2010, "Mass spectrometry study of positive and negative ions in a capacitively coupled
Chapter 6 $H_2O_2$ production with different plasma sources


Chapter 6 H₂O₂ production with different plasma sources


Chapter 7
Conclusions and future works

7.1 Conclusions

Liquid-containing plasmas have attracted much attention recently due to their potential applications in industrial and bio-medical fields. Two types of low temperature atmospheric pressure plasmas in contact with liquid are investigated in this thesis, namely the traditional needle-water but excited at 20kHz plasma and a novel water vapour jet plasma contained in either helium or argon. Both configurations are shown to be suitable for many low temperature medical applications such as sterilisation and wound healing. Physical and chemical characteristics of these two types of plasmas are studied in detail.

7.1.1 Characteristics of needle-water plasmas

Electrical and optical characteristics of needle-water electrode plasmas sustained at 20kHz are investigated in Chapter 3. According to the voltage-current characteristic, there are two working modes: the pulsed and the continuous modes. The plasma is quenched when the voltage polarity changes in the pulsed mode. thus requires large voltage to break down the gas gap in each cycle of the applied voltage. However, there are some species left in the gap
following the quenching the plasma, this reduces the breakdown voltage from its initial value when the gas gap is broke down for the first time. In the continuous mode, the plasma is more intense and always exists in the discharge gap, although it becomes much weaker while the voltage polarity changes. The remaining space charges in the gas gap help re-develop plasmas in the next cycle. Plasma influences the water property such as pH, conductivity and water temperature due to its chemical reactions with water.

A comparative study of AC and DC excited above-liquid plasmas is detailed in Chapter 4. AC plasmas are time-dependent and continuous between different cycles, but DC plasmas are time-independent which need high power to sustain the discharges. AC plasmas can produce 1.2~5 times higher active species than DC plasmas under the same dissipated power. AC excited liquid plasmas have the highest energy use efficiency among the three systems, most of the energy is used to produce useful species not to heat the electrodes and plasmas. The relatively low water temperature under AC needle-water plasmas treatment less than 3 minutes indicates that this type plasma is possible to be safely used on human body.

7.1.2 Characteristics of helium/water vapour jet plasmas

The needle-water plasmas often cause water vaporisation above the gas-liquid interface and this introduces a time-dependence of plasma properties. Yet the relative low concentration of water vapour in the gas gap compromises the production of OH and H$_2$O$_2$ by plasma. In order to overcome the above problems, a needle-ring DBD plasma jet with flowing helium/water vapour gas is studied in Chapter 5. There are four different modes of the needle-ring jet
plasmas, of which a bullet mode and a high current arc mode are investigated in detail. The bullet mode disappears when the moist helium flow rate is higher than 300sccm. Active species production in both the bullet and the high current arc modes increases with increasing water vapour in the gas mixture to a point, but it starts to decrease with further increase of water vapour. Rotational, vibrational and excitation temperatures are shown to be influenced by the moist helium flow rate. Chemical mechanism of active species production is discussed. Electron density plays significant role in producing the active species in the bullet mode. Water vapour concentration together with the electron density in the high current arc mode affects the generation of active species.

### 7.1.3 Hydrogen peroxide production with three plasma sources

Hydrogen peroxide production with AC air needle-saline plasmas, helium/water vapour jet plasmas and argon/water vapour jet plasmas are discussed in Chapter 6. All three plasma sources are effective in producing hydrogen peroxide in saline solution, suggesting that they are suitable for sterilization and wound healing. AC needle-saline air plasmas are not effective when treating the saline solution for more than one minute due to the decomposition of $\text{H}_2\text{O}_2$ via the Fenton reactions. The highest $\text{H}_2\text{O}_2$ production rate is found with the helium jet plasma at 200sccm of the moist helium flow rate in its bullet mode.
Chapter 7 Conclusions and future works

7.2 Future works

Physical and chemical characteristics of two types of low-temperature atmospheric pressure plasmas in contact with liquid are investigated. It is demonstrated that both plasma sources are suitable for sterilization and wound healing. Helium/water vapour jet plasmas are more suitable than AC needle-water plasmas because they are more stable and reproducible in the production of active species. However, helium is expensive, it would be useful to recycle helium for practical applications. The lifetime of OH radicals which is an important agent for biomedical application, is usually short. With the current plasma jet, OH radicals are lost easily before reaching the liquid electrode. There is a need to address this rapid loss of OH radicals. Further biomedical experiments on sterilization and wound healing should be conducted to confirm the effectiveness of the current plasma sources and help develop the experimental setup in the future.

In this thesis, chemical reactions of plasmas in the gas phase are studied in reasonable detail. However, reactions after plasmas entering into the liquid are not well investigated. This is due to the lack of appropriate diagnostics for detection of short-living species in liquid. In order to better control the liquid-containing plasma, it is essential to understand the plasma reactions in the gas phase, the gas-liquid interface and the liquid phase. Furthermore, simulation works should be introduced to help understand the plasma chemical mechanisms.