Plasmas in saline solution

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Abstract. Plasmas created in saline solution are being widely used in many surgical procedures. An overview of the current understanding of the mechanisms leading to plasma production and of the plasma’s effectiveness in removing tissue is presented.

1. Introduction
Plasma production in liquids has largely been confined to those in water. They have been investigated for many decades and those studies have recently been reviewed by Malik et al [1]. There are a huge number of different electrode and power input configurations used to create such plasmas. Most of the plasmas created in liquids to date consist of multiple micro-channel breakdown plasmas, similar to the corona plasma in high-pressure gas plasmas. It appears that the breakdown channel creates a “vapour” channel into which the plasma energy is deposited. This normally requires large voltages (~10kV). In producing plasmas in liquids voltages with the polarity alternating at tens of kHz is found to be most effective and efficient.

There has also been work done on creating a uniform glow plasma in the gas/vapour above a liquid layer which is acting as one of the electrodes of a plasma system [2-5]. This process has been described as “glow plasma electrolysis”. This arrangement is very similar to the gas phase APGDs which are also of increasingly scientific and technological interest.

The focus of this review will be on plasmas created in saline solution by applying moderate (< 300 V rms) bipolar voltage pulses. Interest in such plasmas has been prompted by their ability to ablate tissue in electrosurgical applications. They are currently widely used in various surgical procedures, for example, otolaryngology and arthroscopic procedures [6,7]. The pioneering work of Stalder et al [7-12] on these plasmas forms the basis of much of this overview of plasmas in saline solutions.

2. Plasma formation
Plasma-producing electrosurgical devices which operate in saline solution are manufactured to a wide variety of designs. However the plasma formation in a device such as that shown in Figure 1 can be considered typical although the number, size and configuration of the electrodes may vary from one device to another. Figure 1 shows an 18-electrode surgical probe (ArthroCare 3.5-mm diameter, 90 oriented). Each electrode is 0.38 mm in diameter and 0.38 mm in height. The electrodes are kept in place by an alumina ceramic spacer 3.4 mm in diameter. The spacer is connected to the probe shaft via a stainless steel cap that acts as a common return electrode. Current is induced to flow through the
conductive isotonic saline solution (0.9% NaCl in H₂O) by the application of 100 - 300 V at a frequency of 100-500 kHz, applied from an individual power supply to each individual electrode.

The application of a sufficiently high voltage to the electrodes leads to a stream of bubbles being generated from their immediate vicinity. This is taken to be an indication that vapour layers are formed around the active electrodes. A luminous, orange glow is observed and spectroscopic studies reveal the major emission feature to be the Na atom D-lines at 589 nm. This glow is taken as evidence of the formation of a plasma in the NaCl/H₂O vapour. These assumptions are supported by electrical measurements which show a marked increase in the rms circuit impedance when voltage levels are such that the luminous glow and bubble formation are observed [9].

There are details of the vapour formation that are not yet understood, but Stalder et al [8,9] suggest that if the local ohmic heating of saline solution by the current density near an electrode exceeds the heat of vapourisation of the liquid and the rate at which heat is conducted through the liquid then localized vapour production would be expected. Once a vapour layer is formed the relatively large conductivity of the saline solution and very thin vapour layers combine to create larger electric fields near the electrodes within the layer, compared to where no vapour layers are present. The large electric field E in these thin layers, combined with the comparatively lower number density N of molecules in the vapour with respect to the liquid, produce large reduced electric field values (E/N). These conditions promote electrical breakdown of the vapour and so the formation of a plasma surrounding the electrode. Of course the vapour layer formation will be very sensitive to the liquids electrical and thermodynamic properties.

Time resolved emission studies find that the plasma emission is most intense when the electrode is negatively biased relative to the grounded electrode. This is consistent with electron emission from the electrode and their acceleration in a high E/N environment. Based on a circuit model Stalder et al estimate that, during this part of the rf cycle the electron density in the plasma is about 10¹² cm⁻³ and the electron temperature is between about 4 and 6 eV [9].

3. Kinetics and chemistry.
The ionization threshold of the water molecule is about 13 eV and the excitation threshold is about 7.4 eV. The source of initial excitation and ionisation within the water vapour is therefore via electrons.

Fig.1 Photographs of (a) the tip of an ArthroCare (3.5-mm diameter, 90 oriented) surgical probe, (b) the plasma formed on the probe when energized in saline solution (From reference 9)
with energies of about 10eV. Electrons with energies above about 7.5 eV can dissociate the water molecules into the reactive radicals OH and H with the atomic hydrogen produced with a kinetic energy of about 1eV. Higher energy electrons can produce electronically excited OH (9.5 eV) and H (18 eV). In addition much lower energy electrons can dissociate molecules through dissociative attachment which also produces a negative ion and dissociative recombination with molecular ions. They can also ro-vibrationally excite molecules which can increase the reactivity of the molecules.

At the gas densities associated with the vapour layers a significant proportion of these radicals will react rapidly with one another within the vapour whilst a portion diffuse to the bulk liquid. The higher energy electrons can penetrate many monolayers into the liquid where they become thermalised and hydrated on sub-nanosecond timescales to form solvated (or hydrated) electrons.

The subsequent chemistry in both the liquid and vapour phase is determined mainly by the diffusion processes and the purity of the water used. The radical species and the solvated electrons are all highly reactive species. They will react rapidly with one another and with any other chemical species or materials present in the liquid or at its surface. Volatile species may be formed in the liquid and move across the interface to the vapour. Typically the radical and solvated electron lifetimes are of the order of microseconds.

Stalder et al [10] have used a relatively simple zero-dimension model to explore a number of scenarios in the plasma-induced chemistry of water vapour perturbed by periodic electron-induced dissociation and ionization. Their model consists of a set of 275 vapour-phase reactions involving 45 species derived from various fragments of water and the sodium and chlorine ions in the saline solution. As an example Figure 2 shows the predictions of their model for 100% H2O vapour over a sequence of ionisation events. Note the strong modulation of the electron and ion species, contrasting with the slower build up of plasma-produced products such as H, H2, OH, O2 and H2O2.

![Figure 2](image_url)

**Fig 2.** Mole fractions of the most abundant species in a pure, atmospheric pressure H2O plasma created by repetitive ionization events with an ionization rate of 3.3×10^{19} \text{ cm}^{-3} \text{ s}^{-1}. (From reference 10).
In the presence of solutes (such as biomolecules) oxidation reactions involving reactive and highly oxidising OH radicals are expected to be dominant. In these reactions the OH radical either extracts an electron from the solute molecule to form OH⁻ or in the case of organic molecules (where it behaves as an electrophile) it adds to unsaturated bonds and abstracts H from C-H bonds. In oxygenated water the solvated electrons react with O₂ producing the super oxide radical O₂⁻ which is moderately oxidising and longer lived. The transient intermediate species H and eₐq⁻ are reducing agents.

Free radicals and reactive oxygen species can react with biomolecules like DNA. The solvated electrons, while highly reactive reducing species, are likely only to be of influence in producing and reacting with oxidising species in fast diffusion controlled reactions. It is also important to recognise that the plasma environment produces optical emissions in the visible as well as ultraviolet region. A recent modelling study [10] of plasma-induced cartilage ablation, via depolymerization of collagen, indicated two possible routes could contribute, chemical scission initiated by OH and photochemical decomposition initiated by UV emission from the plasma.

4. Conclusions.

Plasmas produced in saline solution provide a reactive environment that is conducive to their use in a range of surgical procedures. In the past few years an understanding of the plasma formation process and the underpinning plasma chemistry has started to emerge. There is still much to be learnt and many additional applications to be pursued.

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