



(11)

EP 3 122 161 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.01.2017 Bulletin 2017/04

(51) Int Cl.:
H05H 1/24 (2006.01)

(21) Application number: **15177457.7**

(22) Date of filing: **20.07.2015**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
MA

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Remarks:

Amended claims in accordance with Rule 137(2)
EPC.

(54) **JET SYSTEM FOR PLASMA GENERATION IN LIQUIDS**

(57) The invention is related to the jet system for plasma generation in liquids. It consists of a dielectric cylindrical rod with one end conically bevelled. An orifice with the diameter from 0.1 to 2 mm is made along its whole longitudinal axis. A metal electrode is inserted in this orifice so that a free space is created between its end and the conical end of the cylindrical rod. The system further consists of the second electrode which can be coaxially mounted to the ceramic cylindrical rod. One the electrodes is grounded. The cylindrical rod and both electrodes are immersed into the liquid with conductivity of

10-15 000 $\mu\text{S/cm}$. The subject matter of the invention is also the method of plasma generation using the jet. When direct current or alternating current voltage in the range of 50 Hz-2450 MHz is applied, microbubbles are created due to electric current passing through the orifice in the jet. The electric discharge is ignited inside microbubbles when the voltage amplitude is at least 700 V. Microbubbles with plasma inside further expand into the liquid, and an electromagnetic radiation in the wavelength region up to 1100 nm is emitted.

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Description

Field of the invention

[0001] The invention is related to a jet system for plasma generation in liquids.

Background of the invention

[0002] Nowadays, a wide spectrum of systems generating plasma at various conditions is available. Due to the simplicity and related application potentials, electric discharges generated at atmospheric pressure are one of the most important fields. There are many kinds of such discharges these days, and they differ in their principle, electrode configuration and power supplies. Among such discharges, various plasma jets play an important role. In these devices, plasma is blown from a modified capillary into generally gaseous surroundings. Usually, argon or helium with various reactive gas admixtures (nitrogen, oxygen, organic volatile precursors, etc.) are used for plasma generation. A specific situation occurs when plasma of the electric discharge is in contact with liquid because highly energetic reactive species in plasma (electrons, ions, atoms, radicals, etc.) can initiate number of chemical processes in the liquid phase which lead to hardly predictable results.

[0003] Besides electric discharges generated in gases, systems for plasma generation directly in the liquid phase have become a subject of interest in the last few years. In such systems, it is necessary to derive benefit from a strongly inhomogeneous electric field influenced by a substantially high density and different electric properties of liquids. Therefore, typical electrode configurations are point-to-plate or coaxial operated in both polarities. Less typical but also applicable is a pin-hole configuration where electrode spaces are separated by a dielectric barrier made of convenient material and with a small orifice in it. According to the ratio of the barrier thickness to the orifice diameter, we can distinguish a diaphragm discharge (the ratio is approximately one) and a capillary discharge (the thickness is substantially higher than the orifice diameter). Electric discharges generated under the liquid surface (generally containing various conductive solutions) are commonly supplied by pulsing high voltage both in direct current and alternating current regimes up to the microwave region.

[0004] The principle of the electric discharge generation in the liquid phase itself is not fully explained up to now. There are two fundamental theories. The first one, so-called an electron theory, supposes that the breakdown (i.e. the discharge creation) is caused by the same principle as in gases, i.e. by the generation of electron avalanches. Then, the discharge structure is similar to the corona discharge generated in gases. The second theory, so-called thermal, is based on the fact that the liquid is locally heated in regions with high electric field intensity (and thus with high current density). This effect

leads to the formation of microbubbles in which the electric breakdown appears and the discharge is created. Subsequently, the microbubble is expanded. The last results show that except very short pulsing discharges in the orders of nanoseconds, the primary effect is the microbubble generation. On the other hand, there are several results indicating the direct plasma propagation from bubbles into the surrounding liquid in accordance with the electron theory, i.e. by the direct electron ionization of liquid molecules. Independently on the detail breakdown principle itself it can be claimed that plasma in liquids can be generated using various electrode configurations as well as ways of electric supply.

[0005] At present, there are a number of various laboratory setups for plasma generation in liquids. The only known commercially available device is Arthrocare. However, practical experience with this device shows a relatively short lifetime of the main head in which the plasma is generated, and also a relatively small output (units of watts, only) which may not be sufficient for some applications.

Summary of an invention

[0006] Limitations mentioned above can be solved by the jet system for plasma generation in liquids, according to the invention. It consists of a dielectric cylindrical rod which can have one end conical. Along its longitudinal axis, an orifice with the diameter of 0.1-2.0 mm is made in which a metal electrode is inserted from the non-conical end so that a small free space is created between the end of the electrode and the optionally conical end of the dielectric rod. The ceramic cylindrical rod can be partly provided by teflon cover. Further, the rod contains the second electrode which can be coaxially mounted to the ceramic cylindrical rod whereas one electrode is grounded. The cylindrical rod with both electrodes are immersed into liquid with conductivity of 10-15 000 $\mu\text{S}/\text{cm}$.

[0007] The cylindrical rod is preferably made of ceramics or silica glass. The orifice in the cylindrical rod could be cylindrical, conical or of other shape.

[0008] The liquid, in which the cylindrical rod with electrodes is immersed, can be water, water solution of inorganic salt, organic solution or a mixture of water and organic liquid.

[0009] The subject of the invention is also the method of plasma generation in liquids using the jet system according to the invention. On one of the electrodes, voltage of at least 700 V is applied. As the total current must pass through the liquid in the orifice of the cylindrical rod, fast local heating of the liquid occurs in the free space between the end of the rod and the end of the electrode inside the rod, which leads to microbubbles creation. Depending on the geometry and liquid conductivity, the discharge breakdown appears at the definite amplitude of the applied voltage; in general, 700-1300 V is needed for plasma creation inside microbubbles. These bubbles are

further intensively heated by plasma, and as they are spatially limited by the rod size, they expand from the orifice in the rod towards the surrounding liquid. Thus the plasma discharge itself is created which emits electromagnetic radiation with a maximal wavelength of 1100 nm. It is supposed, that the emitted electromagnetic radiation has its bottom bound at 90 nm.

[0010] For the device power supply, both direct (of both polarities as well as stabilized or non-stabilized) and alternating current up to frequencies in the region of microwaves (50 Hz-2450 MHz) can be used, while the supply regime can be pulsing or continual.

[0011] Depending on the power supply, properties of generated plasma are different, and thus consequent processes initiated by the discharge in liquid can also vary. The plasma itself combines a variety of effects which influences the processes in the liquid. Reactive species produced by the electric discharge (in the case of water solutions, especially electrons, atomic hydrogen and oxygen and OH radicals are formed) induce a complicated chemistry both in plasma and in the liquid itself. Chemical processes are also influenced by electrochemical phenomena, especially by electrolysis in the case of the direct current supply regime. Besides, a variety of physical phenomena generated by the discharge can have a synergic action. Among them, we can observe an effect of the strong inhomogeneous electric field at the jet end, electromagnetic radiation including the part in the UV region (OH radical emission with the maximum of 305-315 nm) and VUV region (up to 91-121 nm from the atomic hydrogen), a flux of accelerated bubbles through the liquid from the jet (velocity up to m/s) and shockwaves created by the bubble cavitation when the discharge is quenched. The detailed study of bubbles generation and their propagation was provided using ultrafast camera films.

[0012] The jet system according to the invention is very simple, easy producible and thus cheap. It has a long lifetime and high performance. The jet itself is fast and easily changeable which enables a long-time utilization of the whole system with minimal operation costs. Contrary to plasma jets generated in gases, no systems for gas flow control are required. Further, possibilities of power supplies are extremely wide. It is possible to use various power sources and electric supply modes with the same jet. This provides a wide spectrum of possibilities for various applications. The multi jet system based on the same configuration can be constructed, too.

Brief description of drawings

[0013]

Fig. 1: A schematic drawing of the plasma jet with a conical end and one electrode coaxially mounted into a dielectric cylindrical rod for plasma generation in liquids.

Fig. 2: An example of a plasma micro-jet as a cylindrical rod with plain ends for plasma generation in liquids.

5 Examples of the invention embodiments

Example 1

[0014] According to the Fig. 1, the jet for plasma generation in liquids consisted of a dielectric rod 1 which had one end conically bevelled. Along the whole length of the rod 1, a cylindrical orifice was made in the longitudinal axis. A metal electrode 2 was inserted in the orifice of the rod 1 and tightened into the orifice so that a free space 3 was created between the end of the electrode 2 and the conical end of the ceramic rod 1. The diameter of the orifice in the rod 1 and the electrode 2 was in the range of 0.2-1 mm.

[0015] The second electrode 4 of the system was placed coaxially to the cylindrical rod 1, and due to the safety work, it was grounded. The ceramic cylindrical rod 1 and both electrodes 2 and 4 were immersed into the water solution of inorganic salt (NaCl, KCl or Na₂SO₄) using the distilled water; solution conductivity was in the range of 10-15 000 μ S/cm. For practical and safety work, a part of the cylindrical rod 1 serving for the handgrip was equipped by a teflon cover 5 (Fig. 1).

[0016] After the high voltage application on the second electrode 2, electric current started to flow through the liquid. As the total current must have passed through the liquid in the free space 3 of the orifice in the ceramic cylindrical rod 1, a fast local overheating in this space led to the microbubbles formation. Depending on the above mentioned conditions, the electric breakdown appeared inside microbubbles at the tested voltage range of 1-5 kV. These microbubbles were further intensively heated by the plasma. As they were spatially limited by the orifice in the ceramics, they expanded from the orifice of the ceramic cylindrical rod 1 into the surrounding liquid. Thus, the plasma discharge (jet) itself was created outspreading into the bulk solution, where it initiated chemical and physical processes.

[0017] For this example, following power supplies were used: stabilized direct current voltage where the electrode 2 was either positive or negative, non-stabilized (half-wave rectified) voltage, direct voltage (in both polarities), alternating voltage (50 Hz), high frequency voltage (1-100 kHz) and radio frequency voltage (13.56 MHz). In all cases, the discharge breakdown and stabilized discharge operation was achieved at the amplitude of the applied voltage for at least 5 minutes.

[0018] Estimation of conditions for the discharge breakdown and its energetic consumption was realized by time resolved characteristics of voltage and current over the system. Electromagnetic radiation emitted by the discharge was observed by spectrometry in the range of 200-1100 nm; however, the electromagnetic radiation in the region from 90 nm is also supposed to be emitted.

Creation of bubbles and their velocities were determined by microphotography based on the known exposition time and the microbubbles path length. The detailed study of these processes was provided using ultrafast camera films. Formation of shockwaves was observed just by hearing as well as by records using a piezo-microphone installed under the vessel with the solution in which the jet was immersed. Presence of chemically reactive species (atomic hydrogen and oxygen and OH radical) was confirmed by spectrometric measurements. Hydrogen peroxide, as a stable reactive species, was determined colorimetrically using a selective reaction with peroxotitanyl ion. Efficiency of plasma generated by the jet system according to the invention was proved by organic dye degradation process at selected conditions. Achieved results were in a good agreement with results obtained previously in a common diaphragm discharge. Recently, the multi jet system based on the same configuration was successfully tested.

Example 2

[0019] Instead of the ceramic cylindrical rod 1, a silica glass capillary with the outer diameter of 1 mm was used (Fig. 2). It had a plane end and a cylindrical longitudinal orifice. Experiments at the same conditions as in the Example 1 were carried out using this capillary.

[0020] The jet in such design is applicable as an extender of a catheter or for the treatment of archaeological objects with an extremely broken surface including small cavities. The jet in such design is also possible to insert in very narrow and deep spaces.

Industrial applicability

[0021] The jet system generating plasma in liquids can be utilized directly for the removal of corrosion layers from archaeological objects made mainly of glass and ceramics. Thanks to its size, it is possible to treat broken object surfaces relatively easy or with only a small modification of the side output. Next applications can be found in the field of organic compounds removal from water solutions, especially from those produced by special manufacturing. Further application is a material surface treatment in water and organic solutions, including nanomaterials. Potential applications in the field of organic liquids are also fully opened because they can lead to the formation of new compounds with unique properties. Beyond the technical field, the jet is applicable in medicine, micro-invasive surgery or biological decontamination.

List of reference numbers

[0022]

- 1 - cylindrical rod
- 2 - metal electrode

- 3 - free space
- 4 - second electrode of the system
- 5 - teflon cover

Claims

1. The jet system for plasma generation in liquids, **characterized by** the fact that it consists of a dielectric cylindrical rod (1) optionally with one conically bevelled end, where an orifice with the diameter from 0.1 to 2 mm is made along the whole longitudinal axis of the rod (1), a metal electrode (2) inserted in the orifice from the non-conical end so that a free space (3) is created between the electrode (2) end and the optionally conical end of the cylindrical rod (1); the cylindrical rod (1) is optionally partially provided with a teflon cover (5) and the system further consists of the second electrode (4) optionally coaxially mounted to the dielectric cylindrical rod, (1) while one of electrodes (2) or (4) is grounded, the dielectric cylindrical rod (1) and both electrodes (2) and (4) are immersed into any liquid with conductivity of 10 - 15 000 $\mu\text{S/cm}$.
2. The jet system according to the claim 1, **characterized by** the fact that the dielectric cylindrical rod (1) is made of ceramics or silica glass.
3. The jet system according to the claims 1 to 2, **characterized by** the fact that the free space (3) in the cylindrical rod (1) is cylindrical or conical.
4. The jet system according to the claims 1 to 3, **characterized by** the fact that the liquid is water, water solution of inorganic salt, solution of organic compound or a mixture of water and organic liquid.
5. The method of plasma generation in liquids using the jet system according to the claims 1 to 4, **characterized by** the fact that voltage of at least 700 V is applied on one of electrodes (2) or (4), whereas the induced electric current passes through the liquid in the orifice of the dielectric cylindrical rod (1), in the free space between the end of the rod (1) and the end of the electrode (2) inside the rod (1) microbubbles are created and the electric discharge in these microbubbles is ignited at the amplitude of voltage applied on the electrode (2) or (4), consequently, microbubbles expansion through the orifice in the dielectric cylindrical rod (1) into the liquid induces plasma emitting electromagnetic radiation with the maximal wavelength of 1100 nm.
6. The method of plasma generation according to the claim 5, **characterized by** the fact that direct current voltage or alternating current voltage in the range of 50 Hz - 2450 MHz is applied, whereas the supply

regime is pulsing or continuous.

**Amended claims in accordance with Rule 137(2)
EPC.**

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1. The method of plasma generation in liquids using the jet system consisting of a dielectric cylindrical rod (1) with one conically bevelled end or with both ends non-conical, where an orifice with the diameter from 0.1 to 2 mm is made along the whole longitudinal axis of the rod (1), a metal electrode (2) inserted in the orifice from the non-conical end so that a free space (3) is created between the electrode (2) end and the other conical end or between the electrode (2) end and the other non-conical end of the cylindrical rod (1) and the system further consists of the second electrode (4) while one of electrodes (2) or (4) is grounded, where the voltage of at least 700 V is applied on one of electrodes (2) or (4), **characterized by** the fact the dielectric cylindrical rod (1) and both electrodes (2) and (4) are immersed into any liquid with conductivity of 10 - 15 000 $\mu\text{S/cm}$, whereas the induced electric current passes through the liquid in the orifice of the dielectric cylindrical rod (1), in the free space between the end of the rod (1) and the end of the electrode (2) inside the rod (1) microbubbles are created and the electric discharge in these microbubbles is ignited at the amplitude of voltage applied on the electrode (2) or (4), consequently, microbubbles expansion through the orifice in the dielectric cylindrical rod (1) into the liquid induces plasma emitting electromagnetic radiation with the maximal wavelength of 1100 nm.
2. The method of plasma generation in liquids according to the claim 1, **characterized by** the fact that the liquid is water, water solution of inorganic salt, solution of organic compound or a mixture of water and organic liquid.
3. The method of plasma generation according to the claims 1 to 2, **characterized by** the fact that direct current voltage or alternating current voltage in the range of 50 Hz-2450 MHz is applied, whereas the supply regime is pulsing or continuous.

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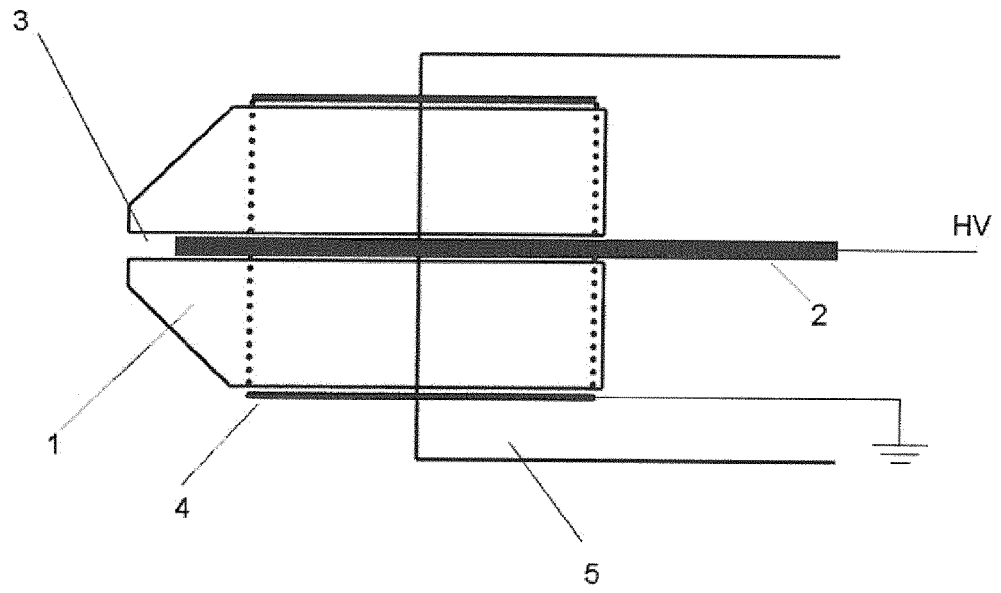


FIG. 1

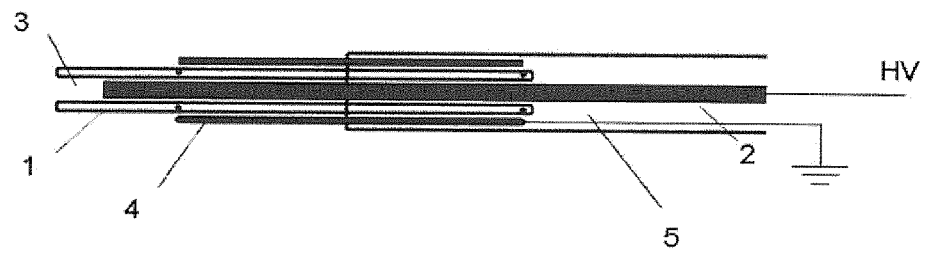


FIG. 2



EUROPEAN SEARCH REPORT

Application Number
EP 15 17 7457

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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 14 December 2015	Examiner Crescenti, Massimo
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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14-12-2015

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