PLASMA OF UNDERWATER ELECTRIC DISCHARGES WITH METAL VAPORS

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This paper deals with spectroscopy of underwater electric discharge plasma with. In particular, the focus is on configuration where the electrodes are immersed in liquid and its application in nanoscience and biotechnology. General overview of the experimental approach adopted by authors aiming to study the water-submerged electrical discharge plasma and effects of various parameters on its properties is described. The electron density was estimated on the base of spectral line broadening and shifting.

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INTRODUCTION

PLASMAS IN LIQUID

Plasmas in liquid are becoming an increasingly important topic in the field of plasma science and technology.

In the last two decades, attention of research on the interactions of plasmas with liquids has spread on a variety of applications that include electrical switching [1], analytical chemistry [2], environmental remediation [3, 4], sterilization and medical applications [5], etc. These opportunities have challenged plasma community with multidisciplinary scientific questions.

Plasmas in liquids usually refer to those systems where the voltage, electric fields or other conditions enable the formation of plasma directly in the liquid phase. Although technologically is very important from many perspectives, the fundamental processes of initiating and sustaining plasma in liquids are poorly understood.

For several years, researchers have been investigating phenomena of electrical breakdown and ionization in liquids. This has led to relatively good understanding of ionization mechanisms in atomic liquids (for example, liquid Ar) [6], while the case for more complex liquids, particularly polar liquids such as water, still requires further study.

Plasmas in liquids have been extensively studied using imaging and optical emission spectroscopy. These diagnostics techniques allow measuring basic plasma parameters including discharge morphology, gas temperature, electron density, and excitation temperatures. Despite of the increased efforts, there remain many unresolved questions about the properties of plasma interaction with liquids. For instance, in [7] authors distinguish and discuss two main challenges: (a) breakdown processes and mechanisms in liquids; and (b) physical and chemical processes occurring at the plasma–liquid interface. The second challenge is particularly multi-disciplinary due to the wide range of chemical species and physical effects which involve radical and reactive species, ions, electrons, UV emission, electric fields, heat and neutral gas flows across the gas–liquid interface. All these individual components are typically studied in distinct fields of research.

PLASMA-LIQUID INTERACTIONS FOR NANOMATERIAL SYNTHESIS

The focus of this paper, in particular, is directed towards a relatively new branch of plasma research, nanomaterial synthesis through plasma–liquid interactions, which has been developing rapidly, mainly due to the various recently developed plasma sources operating at low and atmospheric pressures. Configurations of plasmas over or inside liquids provide plasma–liquid interfaces where numerous occurring physical and chemical processes can be used to synthesize various nanomaterials.

Interactions of nanoparticles with biological environments present a separate interest. Numerous investigations performed in order to define the effect of nanomaterials on crop production [8, 9] have shown that nanoparticles have positive morphological effects, among which enhancement of plant resistance to unfavorable environmental conditions and achievement of high production yields due to the active penetration of nanoelements into the plant cells [10].

Main motivation for the present research lies in the potential biotechnological application of metal colloids as micronutrients. The emphasis of the work is on diagnostics of the water-submerged electrical discharge plasma and effects of metal vapours on its properties. Preceding studies on the subject carried out by authors illustrate a necessity for the further investigations, mostly due to the challenges arising from the data interpretation and complexity of the plasma configuration in terms of its diagnostics [11, 12].

Additionally, authors have previously worked on selection of spectral lines and corresponding spectroscopic data for number of metals (Cu, Ag, Mo, W, Cr) [13, 14] which lays down a foundation for the present study.

1. EXPERIMENTAL APPROACH

Originally, investigations of the underwater electric discharge plasma were initiated with a general objective

to bring better understanding of physical processes occurring during the synthesis of metal colloids by specifically designed electrospark dispersion generator described in [15]. The operation of the latter is based on volumetric plasma-assisted destruction of a liquid-immersed layer of metal granules via simultaneous formation of spark channels in contact points between the granules as a result of pulse energy input from the generator. Despite of the relative simplicity of its operation principle, in practice there are numerous complications to deal with. They mostly originate from impossibility of studying the discharge occurring between two metal granules independently of the overall synthesis process.

Therefore, an alternative experimental apparatus has been designed aiming to 'model' or, in somehow, 'simulate' the behavior of two separately taken granules and discharge between them (Fig. 1). The setup consists of a pulsed generator (I) on the basis of a thyristor-switched capacitor bank, a trigger unit (II) with an adjustable threshold value, a support (III) allowing positioning of the electrodes and a glass container (IV) filled with water. The current is measured with a Rogowsky coil (V), the electrical data is being stored with an oscilloscope (VI). Stochastic movement of metal granules occurring during the operation of setup described in [15] has been considered by allowing pendulum-like motion of one of the electrodes in Fig. 1, while another electrode remain in a fixed position.

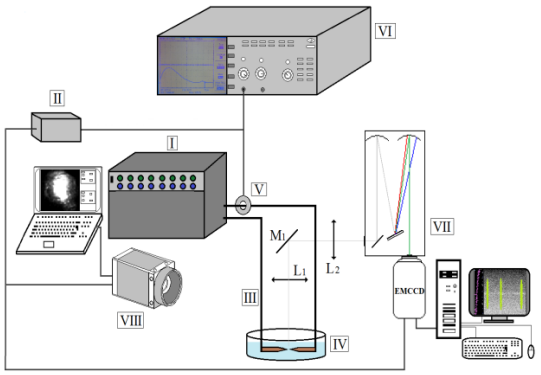

Fig. 1. Experimental setup for the single-pulse underwater electric discharge generation between two electrodes

2. EXPERIMENTAL PARAMETERS SELECTION

The experimental setup (see Fig. 1) was tested by authors to examine its operation capabilities, and results obtained from the first sets of experiments were presented in [11]. This was an initial step with an overall research objective to perform a comprehensive parametric study, and to answer number of questions regarding the plasma discharge characteristics, energy balance of such system and general correlation between its various parameters.

The first challenge occurred with understanding that the adjustment of the electrical operation parameters should be made in order to achieve the correspondence between inter-granules discharge characteristics and that of the inter-electrodes discharge. In [11], the maximal load voltage of the capacitor bank was 430 V for a total capacity of 1000 μF, resulting in the average discharge duration of 320…360 μs. Duration of the discharge occurring between two metal granules was estimated from the high-speed imaging of the process described in [15]. The discharge chamber from the electrospark dispersion generator was connected to the experimental setup in Fig. 1, replacing the electrodes.

The top view of the discharge chamber is shown in Fig. 2. It was visualized using a Photron Fastcam MINI AX100 high-speed camera (VIII, see Fig. 1), the acquisition being synchronized to the discharge triggering. Three configurations were investigated aiming to study the patterns of current passage and sparking process, differing in the amount of the granules placed in the chamber to form a monolayer, a double layer or a triple layer. Also, the granules were of two different sizes: small granules of around 1…2 mm diameter, and those of 3…4 mm diameter. In all cases, high-speed imaging rate was 127500 fps with 128x64 pixels image resolution for current regime of 550 A, corresponding to load voltage of 150 V.

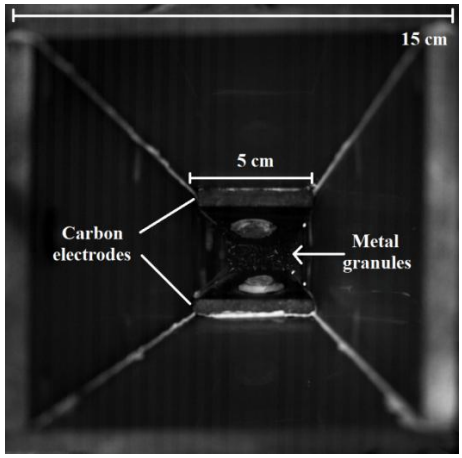

Fig. 2. The top view of the discharge chamber used for the estimation of the spark duration between two metal granules

From the high-speed imaging data, it was concluded that independently of the layer configuration or size of the granules, the average duration of a separate spark discharge is estimated to be 150…180 μs. It was also noted that sparks tend to occur mostly along the carbon electrodes mounted into the chamber's walls rather than in its central region.

Based on these results, the adjustment of the experimental setup in Fig. 1 was carried out. In particular, replacement of the feeding cables by shorter and thicker ones in order to decrease the total resistance, and connecting capacitors in series in order to decrease the overall capacity from 1000 to 330 μF. In such a manner, the average duration of a single discharge between the tips of two electrodes was set up to 150 μs, meeting the target objective.

3. PLASMA DIAGNOSTICS

Due to the often-limited accessibility of active diagnostics and the complicated reactor geometries involving liquids, optical emission spectroscopy (OES)

is the most commonly used to investigate plasmas in liquids. This work is no exception. The spectroscopic diagnostics (see Fig. 1) was performed with an Acton SpectraPro SP-2750 (VII) spectrometer fitted with ProEM 1024 electron-multiplying charge-coupled device (EMCCD) camera (Princeton Instruments). The optical setup is composed of a mirror (M1) and two lenses (L1 and L2), allowing to observe the arc from above. In order to apply OES techniques, plasma must be stable and reproducible, and with 'acceptable' signal-to-noise ratios. The latter can often be improved by the accumulation of data from several measurements.

The first set of experiments carried out with the 'new' adjusted electric parameters allowed to get a glimpse of the setup's performance. For the purposes of a parametric study, as explained before, authors have selected a number of parameters to vary and, respectively, to analyze the results of each parameter's variation. Namely, those of the interest included electrode material (Cu, Mo), type of the liquid (non-purified and deionized water), depth of the electrode immersion (1 and 3 mm water layer above the tips of the electrodes), current input (400, 600, 800 and 1000 A).

Fig. 3 illustrates the emission spectrum of the discharge with current up to 1 kA for the case of Cu electrodes immersed into deionized water. As one can see, the discharge cross section is less than 1.8 mm in diameter with 0.7 mm hot core. Therefore, applying the current up to several hundred amps in such a thin bottleneck leads to high values of current density and, obviously, high electron density in plasma. Traditionally for plasma with metal admixture, the Cu I spectral lines are the most prominent in the emission spectrum. Some copper spectral line are strongly effected by Stark broadening and shift [16]. For such a narrow discharge with high current density, we registered observed along discharge axis line profiles with asymmetric wings for the lines with the most prominent line shift.

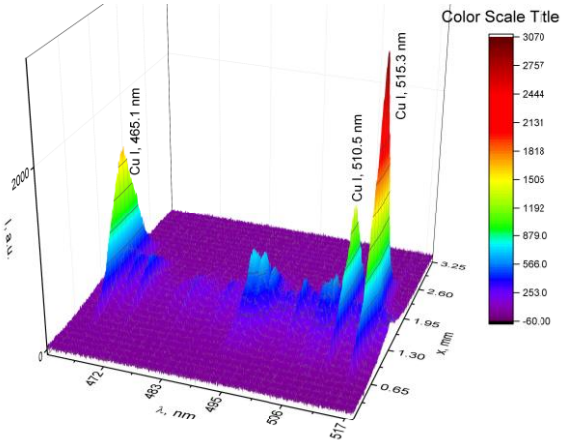

Fig. 3. 3D plot of the emission of the discharge between copper electrodes immersed into deionized water

Fig. 4 shows 3D profile of Cu I 515.3 nm spectral line with pronounced asymmetry at the blue wing for a hot core of the discharge. Such behavior correlates with negative shift data calculated in [16]. Along with this, it significantly complicates line analysis with the aim to obtain plasma parameters data.

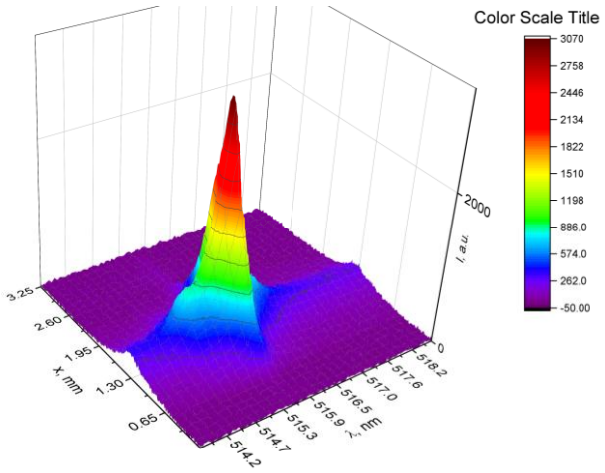

Fig. 4. 3D plot of the Cu I 515.3 nm profile, emitted by the discharge between copper electrodes immersed into deionized water

Taking into account general mechanisms of broadening and shifting, multi-peak fitting of Cu I 515.3 nm line was carried out by Voigt function. Fig. 5 shows observed along discharge axis profile, as well as, multi-peak fitting curves. Results shows line shift from 0.12 to 0.84 nm and line width from 0.23 to 1.27 nm. Electron density was estimated to be in the range from 0.67 to $19.5 \cdot 10^{17}$ cm^{-3} on the base of fitting result data and broadening and shifting constants from [16]. Electron density up to $3.7 \cdot 10^{17}$ cm^{-3} obtained from shift and broadening coincides for peaks 2-4 in Fig. 5, but significantly differ for peak 1 shifting ($19.5 \cdot 10^{17}$ cm^{-3}). Therefore, further experiments and analysis must be carried out to explain such discrepancy.

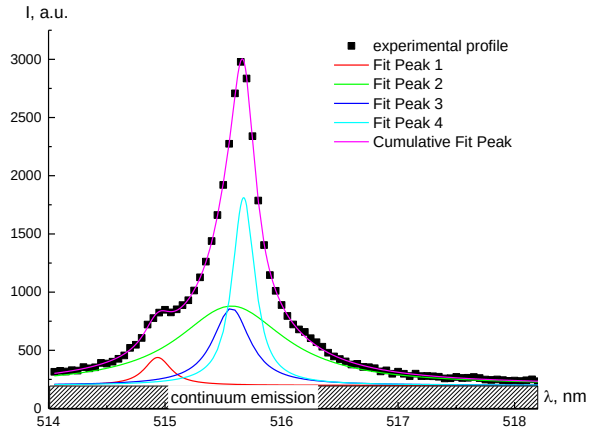

Fig. 5. Observed along discharge axis Cu I 515.3 nm profile, emitted by the discharge between copper electrodes immersed into deionized water

CONCLUSIONS

Model experimental setup was adopted to coincide with xxparameters of plasma reactor for nanoparticle synthesis. Such experimental approach allows to study the water-submerged electrical discharge plasma and effects of various parameters on its properties.

Optical emission spectroscopy was used to estimate electron density range in the discharge between copper electrodes immersed into deionized water.

It was found that emission properties of such plasma source are mainly predetermined by metal vapors admixtures. Line broadening and shifting due to the Stark effect of spectral line Cu I 515.3 nm gave the values of electron density from 0.67 to 3.7 10^{17} cm^{-3}.

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ПЛАЗМА ЭЛЕКТРИЧЕСКОГО ПОДВОДНОГО РАЗРЯДА С ПРИМЕСЯМИ ПАРОВ МЕТАЛЛОВ

В.Ф. Борецкий, А.Н. Веклич, Т.А. Тменова, Я. Крессо, Ф. Валенси, К.Г. Лопатько, Е.Г. Афтандилянц

Рассматриваются особенности спектроскопии плазмы подводного электрического разряда с примесями паров металлов и его применения в нано- и биотехнологиях. В частности, исследуется разряд, возникающий между двумя погруженными в воду металлическими электродами. Приводится детальное описание экспериментальной методики по реализации спектроскопической диагностики плазмы такого разряда. Концентрацию электронов оценили на основе расширения и сдвига спектральной лини.

ПЛАЗМА ЕЛЕКТРИЧНОГО ПІДВОДНОГО РОЗРЯДУ З ДОМІШКАМИ ПАРІВ МЕТАЛІВ

В.Ф. Борецький, А.М. Веклич, Т.А. Тменова, Я. Крессо, Ф. Валенсі, К.Г. Лопатько, Є.Г. Афтанділянц

Розглядаються особливості спектроскопії плазми підводного електричного розряду з домішками парів металів та його застосування в нано- та біотехнологіях. Зокрема, досліджується розряд між двома зануреними у воду металевими електродами. Наводиться детальний опис експериментальної методики з реалізації спектроскопічної діагностики плазми такого розряду. Концентрацію електронів оцінили на основі розширення та зсуву спектральної лінії.