# Emission Spectroscopy of Underwater Discharge Plasma in the Synthesis of Metal Nanoparticles

Murmantsev O.O.[1], Ninyovskij V.V.[1], Veklich A.M.[1], Boretskij V.F.[1], Lopatko K.G.[2]

[1]Faculty of Radio Physics, Electronics and Computer Systems, Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska str., Kyiv, 01601, Ukraine

[2]National University of Life and Environmental Sciences of the Ukraine, Kyiv, Ukraine

E-mail: murmantsev.aleksandr@gmail.com

***Introduction.*** The process of electric erosion, caused by gas discharge between metal electrodes immersed in a liquid, is one of the most interesting methods for generating metal nanoparticles. These methods have gained special attention due to their potential use in sterilization, treatment, and the production of materials for various fields such as medicine and agriculture. It is nature that to improve the characteristics and properties of solutions with nanoparticle it is necessary to investigate directly the process, which occurs during nanoparticles formation. Namely, the plasma of discharges, which burns between granules used as a source of metal particles in the obtained solutions, should be understudy. The most suitable approach to such investigation is optical emission spectroscopy. On the one hand, this method enables to obtain with sufficient accuracy the main plasma parameters, such as temperature and electron density, which characterise the processes of nanoparticles formation. On the other hand, such technique does not perturb the plasma and cannot affect the properties of the resulting product. Therefore, this work focuses on the diagnostics of such a kind of underwater discharge plasma using optical emission spectroscopy. In this work the underwater discharges between various metal granules (namely zinc, iron and copper) have been investigated. Additionally, for the discharges between iron granules the four different discharge conditions have been studied, namely the discharges in pure distill water, in water with air flow, in electrolyte and in the electrolyte with air flow.

***Experimental investigation.*** The synthesis of metal nanoparticles in a liquid medium was carried out using a specially developed setup, as shown in Fig. 1. The setup consisted of a discharge chamber filled with deionized water, in which cylindrical metal granules were placed. The discharge chamber was connected to an impulse generator, which was powered by a single-phase 220 V alternating current network with a frequency of 50 Hz. The input voltage was rectified and filtered using a combination of power diodes (VD1 and VD2) and thyristors (VD3 and VD4). The input energy was stored in a working capacitor (C1) with a capacitance of 50 μF. The spark microdischarges between random pairs of metal granules were initiated by rapidly switching the thyristor VD5. The timing of the switching moment for this thyristor was controlled by the half-period of free oscillations of the LC2 oscillatory circuit.

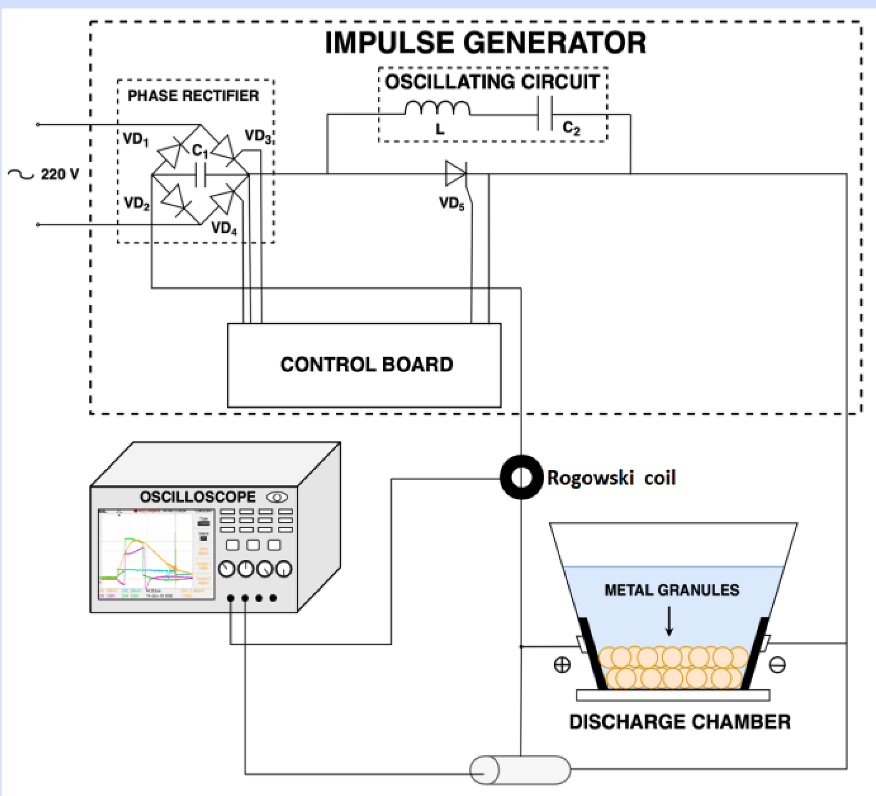


*Fig. 1. Experimental setup for underwater electric discharge investigation*

The emission spectra in the range of 440 to 910 nm were recorded using the Solar LS SDH-IV spectrometer positioned in front of this window.

| Metal | $N_e[m^{-3}]$ |
|---|---|
| Copper in water | 9.5E+22 |
| Zinc in water | 1.5E+23 |
| Iron in water | 8.4E+23 |
| Iron in water with air flow | 1.1E+24 |
| Iron in electrolyte | 5.4E+23 |
| Iron in electrolyte with air flow | 1.7E+24 |

*Table 1*

***Results and discussions.*** The typical spectra of plasma registered in underwater discharges between various metal granules (namely iron, copper, and zinc) are shown in Fig. 2. All spectra are normalized by the exposure time, which was 250 ms, 300 ms, and 10 ms for plasma with zinc, iron, and copper vapour, respectively (no spectral sensitivity is taken into account). A significant difference in emissions can be observed between plasma with different metal vapours. Specifically, plasma of underwater discharges between copper and zinc granules exhibits a purely linear spectrum, while the plasma with iron vapour shows a perceptible continuum in the spectral range of 500-550 nm. This continuum is likely a recombination continuum, indicating a significant electron density in the discharge plasma between iron granules.

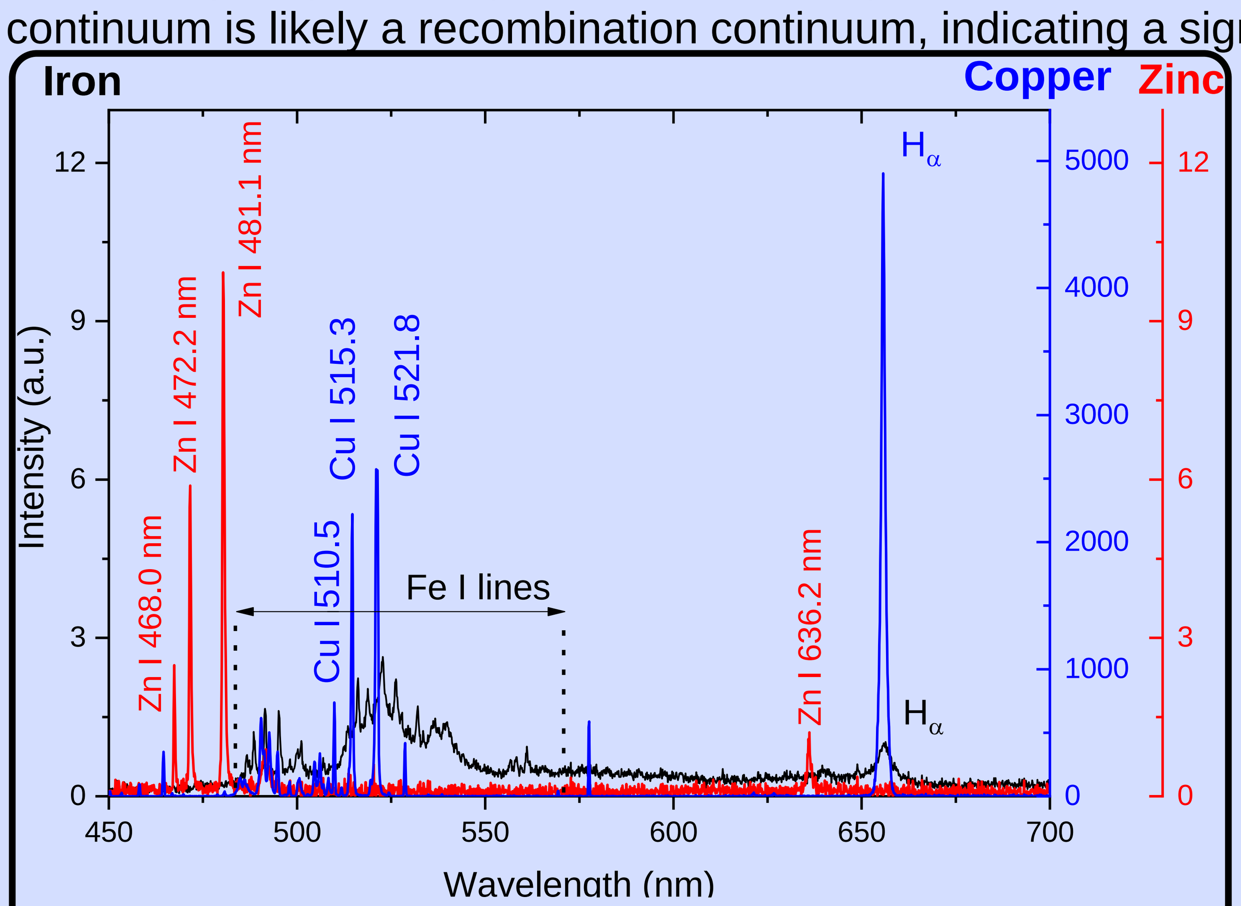


*Fig. 2. Emission spectra of underwater discharge plasma between zinc (red), copper (blue) and iron (black) granules*

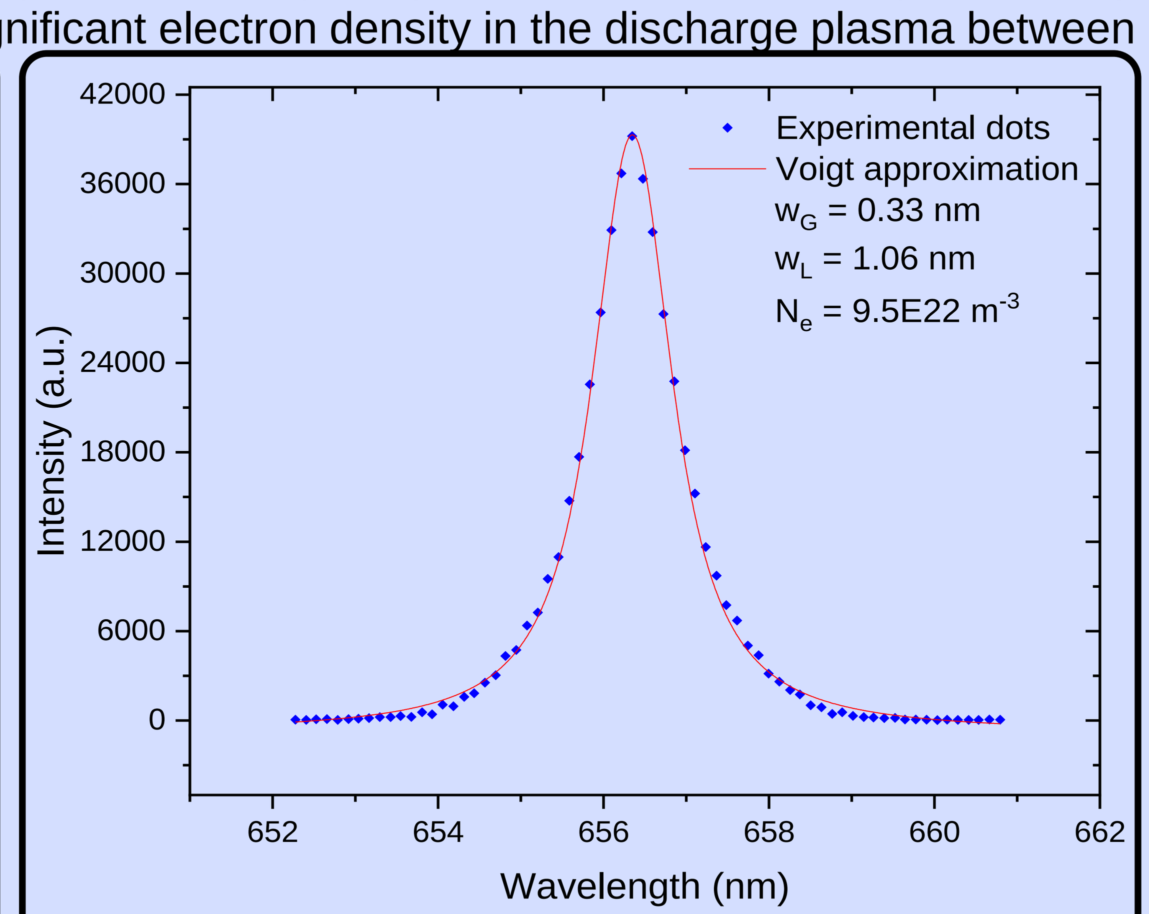


*Fig. 3. Typical approximation of $H_\alpha$ spectral line in plasma with copper vapour admixtures*

Another notable difference is the absence of the $H_\alpha$ spectral line of the Balmer series in the spectrum of zinc, suggesting that the energy applied to the chamber mainly targets the destruction of zinc granules and is not dissipated in the aquatic environment. On the other hand, in the spectrum of copper, the $H_\alpha$ line predominates in intensity, suggesting a significant dissipation of energy in water. In the spectrum of iron, the $H_\alpha$ line is not intense, but its width is noticeably larger compared to the same line in the spectrum of copper. This, along with the presence of a recombination continuum, indicates a significant electron density in the plasma of an underwater discharge between iron granules. The electron density in the plasma was determined using the full width at half maximum (FWHM) of the $H_\alpha$ spectral line, which is supposed to be broadened due to the Stark effect. Additionally, in the case of plasma with copper vapour admixtures, the electron density was also calculated from the width of the Cu I 515.3 nm spectral line. A typical approximation of the $H_\alpha$ spectral line is shown in Fig. 3. The electron density obtained from the FWHM of the Cu and $H_\alpha$ spectral lines coincided ($9.5{\cdot}10^{22}$ and $8.4{\cdot}10^{22}$ $m^{-3}$, respectively).

The emission spectra of the plasma of underwater discharge between iron granules for four different modes are shown in Fig. 4(a). One can observe that discharges in pure water are characterized by low intensity of the emission spectrum of plasma. The discharges between iron granules in pure water are characterized by plasma with the least intense radiation. By adding air flow, the intensity increases, just as when replacing water with electrolyte. The most intense radiation is observed in the discharge plasma in the electrolyte when an air flow is added. An increase in the intensity of the recombination continuum is also observed, which indicates an increase in the electron density. Typical profiles of the $H_\alpha$ line and its approximation in the plasma of underwater discharges between iron under different conditions are shown in Fig. 4(b). The determined electron concentrations are shown in Table 1.

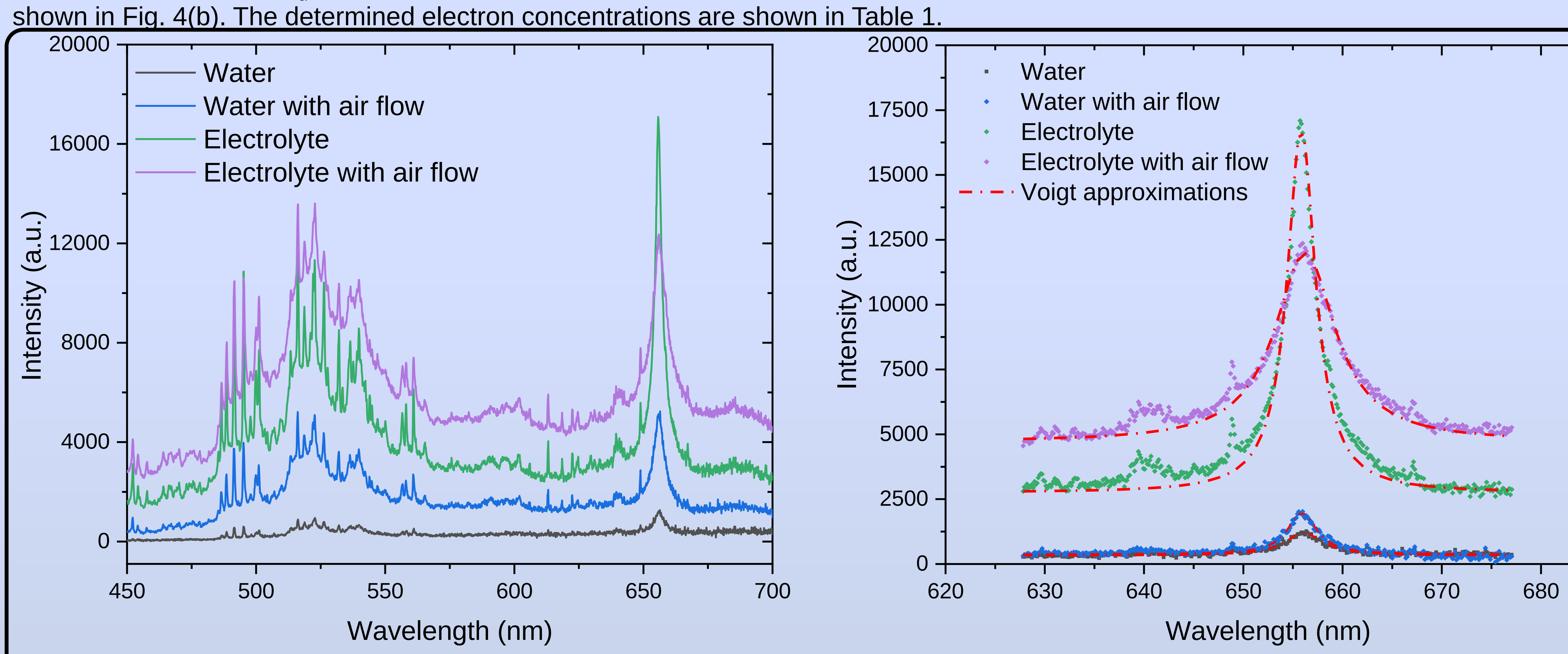


*Fig. 4. Emission spectra (a) and profiles of $H_\alpha$ spectral line in discharge plasma between iron granules under different conditions*

***Conclusions***. The plasma of underwater discharge between various types of metal granules, namely zinc, iron, and copper, was investigated. It was found from the emission spectra of the corresponding materials that plasma with zinc vapours is characterized by the absence of the $H_\alpha$ spectral line. This suggests that, due to the low melting point of zinc, the majority of the applied energy primarily targets the destruction of zinc granules and is not dissipated in the aquatic environment. On the other hand, in the case of copper granules, a portion of the applied energy is dissipated in water, as evidenced by the significant emission intensity of $H_\alpha$. However, the electron density determined from the $H_\alpha$ FWHM is the lowest in comparison with the cases of zinc or iron granules. This indicates that a smaller portion of the energy is directed towards ionizing the metal.

In contrast, the discharge plasma between iron granules is characterized by a significant electron density compared to plasma with zinc or copper vapour admixtures. This is evidenced by a substantial broadening of the $H_\alpha$ line in such plasma, as well as the presence of a recombination continuum. It can be concluded that a significant part of the energy applied to the chamber filled with iron granules goes towards the destruction of the granules with subsequent ionization of metal atoms in the plasma.

Moreover, in the case of iron granules, four different discharge conditions have been examined, including discharges occurring in deionized water, water with air flow, in an electrolyte, and an electrolyte with air flow. It was found that the replacement of pure water with an electrolyte, as well as the addition of an air flow, leads to an increase in both the intensity of the spectral lines and the electron density. Further research is needed to determine the causes of these effects.