X International conference

Plasma Physics
and
Plasma Technology

Contributed papers

Minsk, Belarus
September 12 – 16, 2022

B.I. Stepanov Institute of Physics
National Academy of Sciences of Belarus

The National Academy of Sciences of Belarus
B.I. Stepanov Institute of Physics of the National Academy of Sciences of Belarus
Joint Institute for High Temperatures of the Russian Academy of Sciences

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(PPPT-10)

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CONTRIBUTED PAPERS

Minsk
«Kovcheg»
2022

UDC 533.3(082)

EDITORS:
N.V. Tarasenko, A.A. Nevar, N.N. Tarasenka, M.S. Usachonak

Proceedings of the X International Conference «PLASMA PHYSICS AND PLASMA TECHNOLOGY» (PPPT-10): September 12-16, 2022, Minsk, Belarus / Edited by N.V. Tarasenko, A.A. Nevar, N.N. Tarasenka, M.S. Usachonak - Minsk : Kovcheg, 2022. – 520p.

ISBN 978-985-884-193-5

ATMOSPHERIC PRESSURE PLASMA-ASSISTED FABRICATION OF IRON OXIDE NANOSTRUCTURES

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In the last decade, the special interest of researchers has been focused on the synthesis and study of the properties of iron oxide and oxyhydroxide nanoparticles in view of the prospects for their practical applications [1-3]. One of the methods for such structures obtaining is the low-temperature plasma electrolysis based on a glow discharge at atmospheric pressure between a metal and liquid electrodes.

Although the exact mechanisms of the nucleation and growth of nanoparticles in the plasma of a glow discharge with a liquid electrode remain not fully understood, it is obvious that this occurs due to the reduction of the ions in liquid to atoms, their combination into clusters, and the subsequent growth.

The process of nanoparticle synthesis can divide into two stages: nucleation and growth. During plasma initialization, a large number of free electrons and high-energy particles are formed at the interface between the plasma and the solution, which cause the activation of metal ions and lead to a rapid nucleation process in this region. Nascent atoms in collisions grow into larger nanoparticles, which leave the "reaction zone" and fall into a solution with a lower concentration of ions. Once far from the zone of nucleation and diffusion, without a sufficient amount of activated raw material, the nanoparticles stop their growth and settle to the bottom.

Recently [1,3] it was shown that in the pulsed discharge with a liquid electrode, the synthesis of iron oxyhydroxide nanoparticles mainly occurs due to the redox properties of active particles formed in the plasma discharge. The synthesis mechanism described by these authors showed that the hydroxyl radical formed during the discharge plays a decisive role in this process.

In the present work, experimental studies of the process of formation of iron oxide nanostructures by low-temperature plasma electrolysis, including spectroscopic studies of plasma in contact with a solution and characterization of the structure and composition of formed nanoparticles, were carried out. The method of low-temperature plasma electrolysis is based on a glow discharge at atmospheric pressure between metal and liquid electrodes. The metal electrode was a stainless steel capillary through which argon was supplied (flow rate ~ 20 ml/min). The outer diameter of the electrode was 800 μm, and the inner diameter was 500 μm. The gas flow was regulated using a leak valve. The electrode was located at a distance of 2–6 mm from the liquid surface. An iron sulfate solution with a graphite electrode immersed in it served as a "liquid electrode". The discharge was powered from a stabilized direct current source with a maximum

voltage of 3.6 V. The discharge current varied during the experiments from 3.2 to 5.6 mA. As the power supply voltage increased, the discharge gap between the surface of the solution and the electrode end brokes down, and a glow discharge of atmospheric pressure was ignited. The stable state of the plasma was ensured by selecting the parameters of the discharge circuit and the rate of the argon flow.

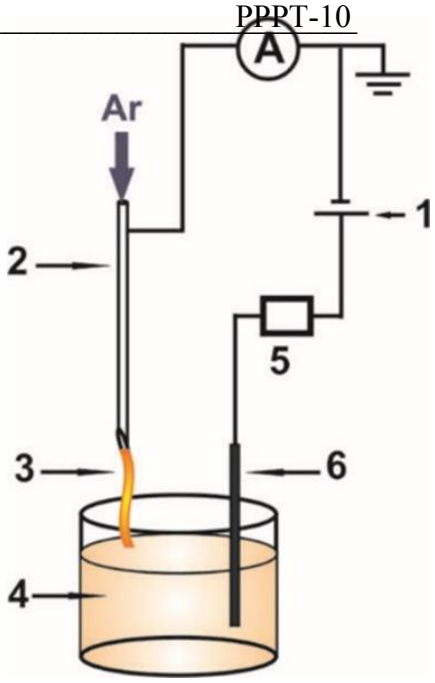

Fig. 1. Experimental setup: 1 - power supply, 2 - needle, 3 - plasma, 4 - ferrous sulfate solution, 5 - resistor, 6 - graphite electrode

Both the modes : mode 1 (needle - "anode", liquid - "cathode") and mode 2 (needle - "cathode", liquid - "anode") were investigated in the work.

The results of spectroscopic studies of a plasma jet generated in an argon flow between metal and liquid electrodes are shown in Fig. 2-4. The main emission of the glow discharge is concentrated in the spectral range of 300–400 nm and is represented by the bands of hydroxyl OH(X-A) and the second positive system of the nitrogen molecule N_2 (337.1 nm (0 - 0) with the most intense emission band and the less intense bands 357.7 (0 - 1), 375.5 (1 - 3), 380.5 nm (0 - 2)). In the visible region of the spectrum, the spectral line of the hydrogen atom Hα (656.28 nm), Hβ (486.133 nm) and argon lines were observed. We note that it was not possible to detect the emission of iron atoms, most likely due to the insufficiently high plasma temperature and high excitation energies of the upper levels of iron atoms.

The temperature estimation methods used in our work are based on the search for the best fit between the experimental and simulated emission spectra of OH radicals or the second positive N_2 system. Fig. 2-3 show an approximation of the N_2 and OH (in insets) spectra by a theoretically calculated ones for estimating the vibrational and rotational temperatures of the plasma. The difference between the vibrational (~2800 K (mode 1) and ~3000 K (mode 2)) and rotational (~900 K (mode 1) and ~850 K (mode 2)) temperatures indicates a non-equilibrium state of the microplasma of this type of discharge. The gas temperature (rotational temperature Trot) calculated from molecular spectra is in good agreement with the data of [4], where the discharge conditions are similar (discharge at atmospheric pressure in argon at a current of several mA).

A widely used method for estimating the temperature of plasma electrons is the method of relative intensities of spectral lines [5]. However, suitable emission lines for determining the electron temperature of the plasma from the ratio of atomic lines with different excitation energies or atomic and ion lines in the discharge emission spectrum have not been found.

Therefore, when estimating the electron concentration from the broadening of spectral lines, it was assumed that the electron temperature in our experiment is about 10,000 K, similar to the electron temperature estimated in [4].

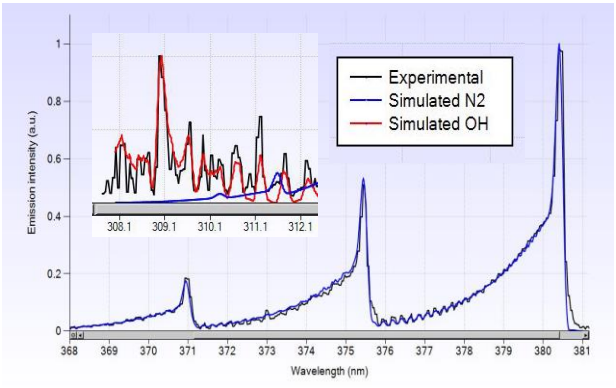

Fig. 2. N_2 and OH (in inset) spectra approximated by the theoretically calculated spectrum (mode 1, Tvib = 2800K, Trot = 900K)

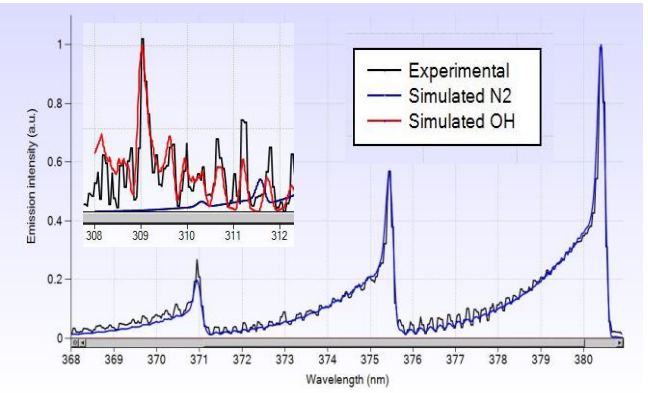

Fig. 3. N_2 and OH (in inset) spectra approximated by the theoretically calculated spectrum (mode 2, Tvib = 3000K, Trot = 850K)

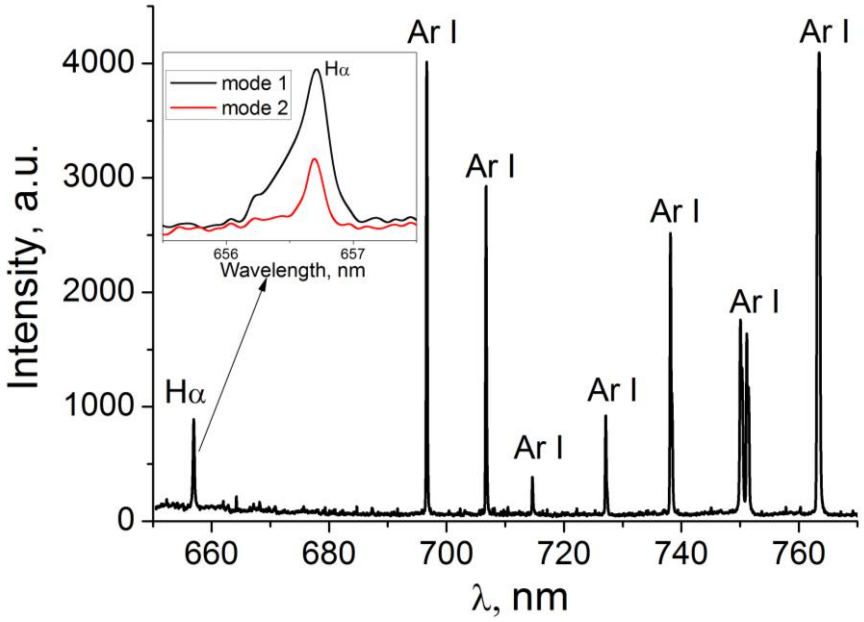

Fig. 4. The emission spectrum of the discharge plasma in the region of 650 – 770 nm. Inset – enlarged region with Ha

The electron concentration was determined from the measured Stark width of the hydrogen atomic line Ha 656.28 nm (Fig. 4) [6]. The electron density was $8.02 \cdot 10^{15}$см$^{-3}$ (mode 1) and $5.9 \cdot 10^{14}$см$^{-3}$ (mode 2).

To investigate the effect of polarity of discharge on the morphology and composition of nanoparticles formed, the SEM images and EDX mapping were performed using SUPRA 55WDS (Carl Zeiss, Germany) microscope. SEM images (Fig. 5) reveal that the samples consist of hierarchical urchin-like spheres (up to 1μm) assembled from nanorods. When the needle acts as an anode (Fig.5a),

particles are composed of subunits with small (less 100 nm) needles. In this case the length of the needles reaches up to 0.5 μm.

EDX spectra (not presented) confirmed that the obtained samples mostly consist of iron and oxygen with the presence of trace amount of sulfur.

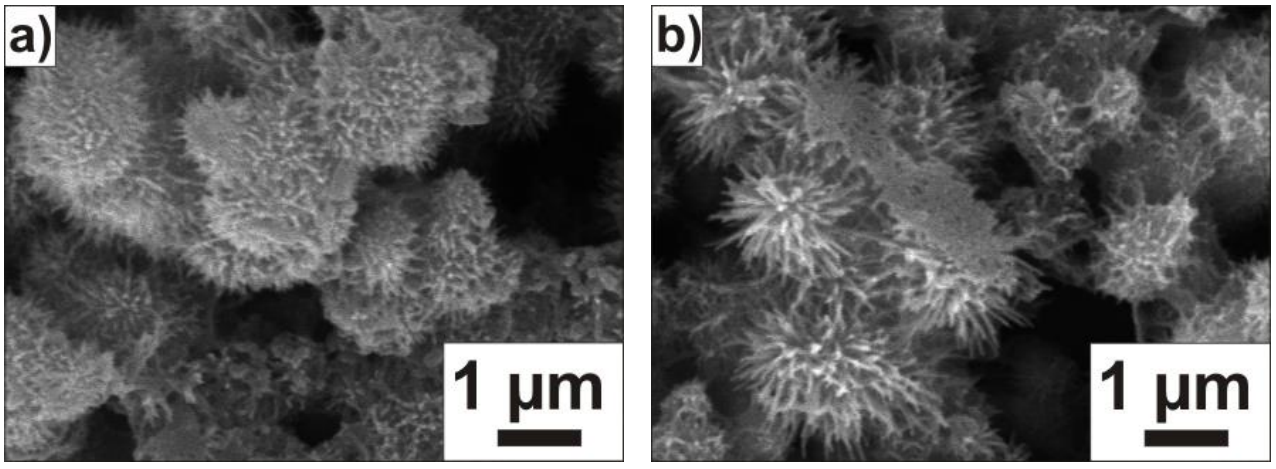

Fig. 5. SEM images of urchin-like spheres synthesized at atmospheric pressure discharge in contact with solution in mode1 (a) and mode 2 (b)

In summary, the iron oxyhydroxide nanoparticles were fabricated via glow discharge at atmospheric pressure between metal and liquid electrodes. It has been established that the polarity of the electrodes affects to the characteristics of the plasma and the morphology of the synthesized particles. Further research will focus on studying the electrochemical characteristics of hierarchical urchin-like FeOOH spheres in anodes for lithium-ion batteries.

Acknowledgements. This work was supported by the National Academy of Sciences of Belarus (project Convergence 2.2.05), by BRFFR (grant number F21RM-104) and by RFBR (grant number 20-53-04010).

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