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FERROCENE DISPROPORTIONATION REACTIONS IN A PLASMA-LIQUID SYSTEM WITH A ROTATING GLIDING DISCHARGE

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A plasma-liquid system with the activation of H_2O distillate and 0.1 M ferrocene solution in organic solvents (ethanol, acetonitrile) with a rotating gliding discharge plasma was studied. The research was conducted using various plasma-forming gases (air, Ar, N_2, CO_2). Determination of plasma parameters was performed by plasma emission spectroscopy methods. It was shown that the plasma of both the rotating gliding discharge and the plasma of the secondary discharge supported by the gliding discharge are non-isothermal. The study of the physicochemical properties of the synthesis products was performed by adsorption, luminescence analysis, polarimetry, chromatography-mass spectrometry and NMR methods. It was found that cyclopentadiene ligands of ferrocene disproportionate into saturated cyclic hydrocarbons (cyclopentane and pentane). Also, as a result of plasma chemical synthesis, aromatic compounds (benzene and its derivatives) are formed.

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INTRODUCTION

High-molecular compounds are the basis of many modern materials and technologies. However, their transformation or conversion through chemical reactions is a difficult task because they have high thermal stability and complex molecular structure.

The study of plasma technologies within the framework of high-molecular compounds conversion is important because it can open the door to new technology and methods that can help solve the problems associated with the processing of these complex materials. It can also contribute to better understanding of the fundamental processes that occur during the interaction between plasma and high-molecular compounds.

The paper is aimed at researching the potential of plasma technology as a possible solution to this problem, as well as the plasma characteristics under which it will be possible. A plasma-liquid system for processing solutions of high-molecular organic and inorganic compounds was used for our study [1]. The system is based on a rotating gliding discharge directly immersed in the liquid [2]. This method can enable the efficient transformation of high-molecular compounds into lower molecular weight compounds that can have many useful applications.

1. THE EXPERIMENT

1.1. DESCRIPTION OF THE DEVICE FOR LIQUIDS PROCESSING AND SAMPLING

An experimental setup with a rotating gliding discharge immersed in a liquid [1] is presented in Fig. 1. The plasma generator consists of a central electrode (cathode), an upper flange (anode) and a dielectric chamber with holes for tangential supply of the working gas. The central part of the anode has a conical shape with a hole in the center. The diameter of the hole is 3 mm. A rotating gliding discharge is ignited between the cathode and the anode. The distance between the cathode and the anode is 1 mm. A quartz tube is placed on the anode, into which the test liquid is poured. A flange is placed on top of the quartz tube, into which an annular secondary discharge electrode is mounted, which was immersed in liquid. As the working gas were used air, Ar, N_2 or CO_2, the flow amounted to 10 and 15 l/min. The gas was fed tangentially to the system axis. The system outlet was connected to the ventilation system.

BP 100 and BP 150 sources with a voltage ripple factor of 10% at a frequency of 100 Hz were used as power sources for discharges.

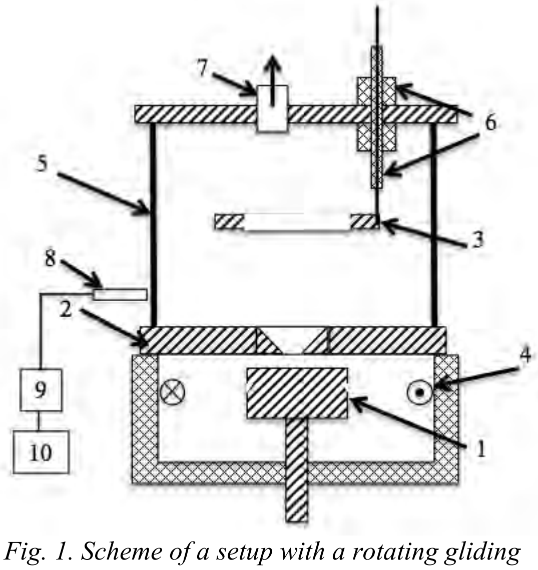

Fig. 1. Scheme of a setup with a rotating gliding discharge immersed in a liquid:
1 – high-voltage primary discharge electrode; 2 – grounding electrode; 3 – high-voltage secondary discharge electrode; 4 – gas inlet; 5 – quartz cylinder; 6 – dielectric; 7 – gas outlet; 8 – optical fiber; 9 – spectrometer; 10 – PC

H_2O distillate and solutions of inorganic and organic compounds were used as the test substances which were processed in plasma-liquid systems. Crystallized inorganic substances of ammonium molybdate ($(NH_4)_2MoO_4$), nickel chloride ($NiCl_2$), cobalt chloride

($CoCl_2$) were diluted in distilled water. Organic substances were diluted in ethanol and acetonitrile. The substances used were *benzotriazole ($C_6H_5N_3$) and ferrocene ($C_{10}H_{10}Fe$)*. 100 ml of solution was poured into the system for processing.

1.2. METHODS OF MEASURING DISCHARGE PARAMETERS, PLASMA AND OUTPUT PRODUCTS

The volt-ampere characteristics (VAC) of the discharges were measured using an INSTRUSTAR-ISDS205A oscilloscope, the signals to which were fed from an ohmic-capacitive voltage divider D (1/10.000) and measuring resistors of 50 Ω (Fig. 2).

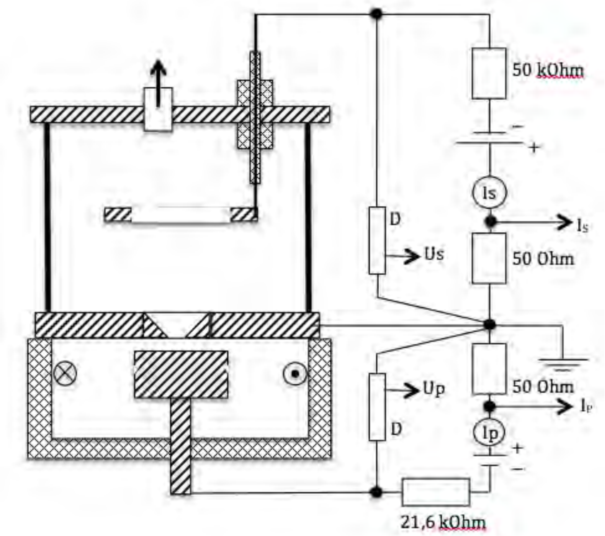

Fig. 2. Discharge powering scheme

Determination of plasma parameters of both independent rotating gliding discharge and secondary discharge was carried out using UV and visible emission spectroscopy of plasma (200…1.000 nm). Registration of radiation spectra was performed using the Solar TII spectrometer. The values of the temperatures of the population of the electron levels of the atoms T*e, the vibrational levels of the molecules Tv and the rotational levels of the molecules Tr were determined by the dependence of the temperatures of the population of the corresponding levels of the O atom and the OH and N_2 molecules on the ratio of the radiation intensities Ii/Ik at two wavelengths – λi, λk. These dependences were built based on the results of simulation by the SPECAIR code [3] of the O, N_2 radiation spectra of the band system (C-B) and the OH band system (A-X) in the temperature ranges 500…20.000 K, taking into account the experimentally determined slit function of the Solar TII spectrometer (Gaussian contour 0.3 nm wide at half height). It should be noted that the difference between the shapes of the inseparable multiplet of 9 lines of oxygen (926 nm) in the measured and simulated spectra does not exceed 5%. The relevant dependences $T(I_i/I_k)$ are shown on Fig. 3 for T*e O λ_i = 844 nm, λ_k = 777 nm and λ_i = 926 nm, λ_k = 777 nm; on Fig. 4 for Tr (OH) λ_i = 306.7 nm, λ_k = 308.9 nm; on Fig. 5 for Tr (N_2) λ_i =336 nm, λ_k = 337 nm; on Fig. 6 for Tv (N_2) λ_i =315 nm, λ_k = 337 nm.

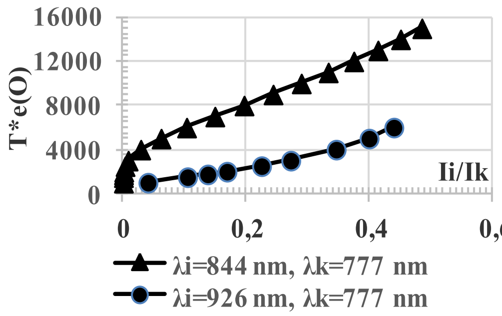

Fig. 3. Dependence of the temperature of the O I electron levels population on the ratio of intensities of inseparable multiplets with λ = 777, 844, 926 nm

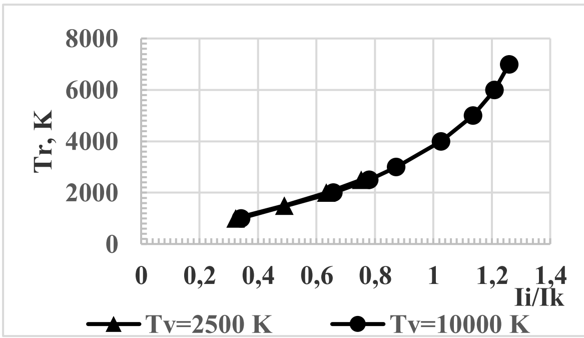

Fig. 4. Dependence of the temperature of the OH rotational levels population on the ratio of intensities in the band (A-X) at λi = 306.7, λk = 308.9 nm

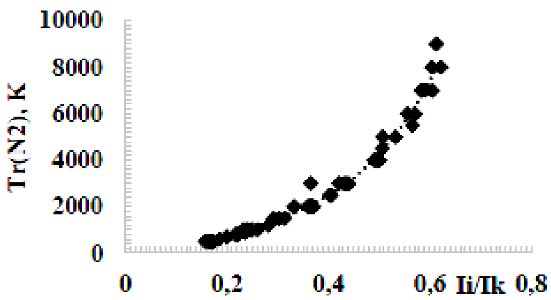

Fig. 5. Dependence of the temperature of the N_2 rotational levels population on the ratio of intensities in the band (0-0) of the 2+ system at λi = 335.9, λk = 336.9 nm

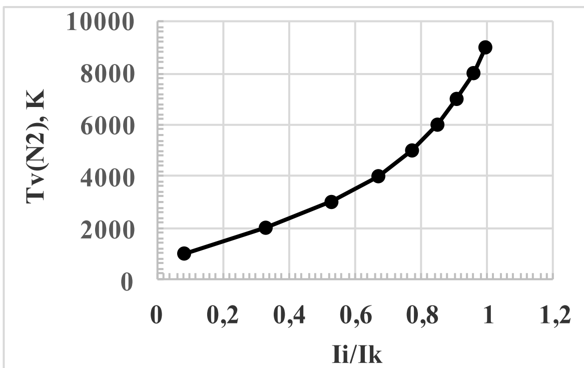

Fig. 6. Dependence of the temperature of the N_2 vibrational levels population on the ratio of intensities in the 2+ band system at λi = 315, λk = 337 nm

The analysis of reaction mixtures of ferrocene on benzotriazole was performed using nuclear magnetic resonance on a Bruker-400 device on ^{1}H nuclei.

2. RESULTS AND DISCUSSION

2.1. ELECTROPHYSICAL PARAMETERS OF DISCHARGES

Volt-ampere characteristics of discharges (Figs. 7, 8) measured by pointer instruments are presented for the primary and secondary discharges when the system is filled with distilled water, the volume of which was equal to 100 ml.

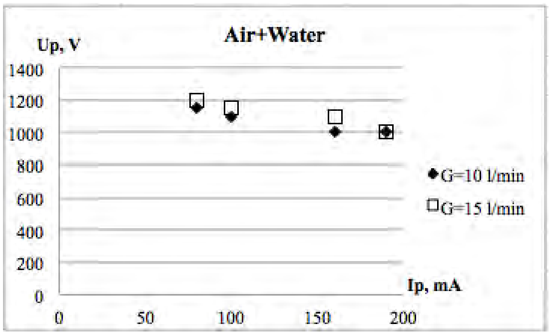

Fig. 7. Volt-ampere characteristics of the primary discharge at air flows of 10 and 15 l/min

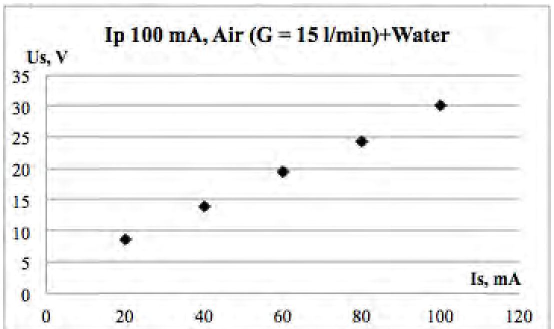

Fig. 8. Volt-ampere characteristics of the secondary discharge at a current Ip of 100 mA

The VAC of the primary discharge has a decreasing nature and, within the measurement error, does not depend on the gas flow rate. The VAC of the secondary discharge has a linear nature within the studied current range.

For a more accurate VAC measurement, an INSTRUSTAR–ISDS205A oscilloscope was used. Typical oscillograms of current and voltage drop on a gliding discharge at an air flow rates of 10 and 15 l/min are shown in Figs. 10 and 11. It can be seen from the oscillograms that current and voltage have constant and variable components. It also made it possible to determine how the current and voltage signals change over time with a fixed constant component of the discharge current. Current fluctuations amount to ± 15 mA.

In turn, the variable component of the current is a superposition of a sinusoidal component with a frequency of pulsations of the power source (100 Hz) and a sawtooth component with a frequency (3 kHz at G = 10 l/min) depending on the gas flow rate, which is characteristic of discharges with transverse blowing [4]. Also, the shape of the sawtooth component is affected by the gas flow rate.

Fig. 9 shows the VAC of the primary discharge for different air flows determined by sections of the oscillograms corresponding to the rise and fall of the current at a time interval of 5 ms for the plasma-liquid system with H_2O distillate.

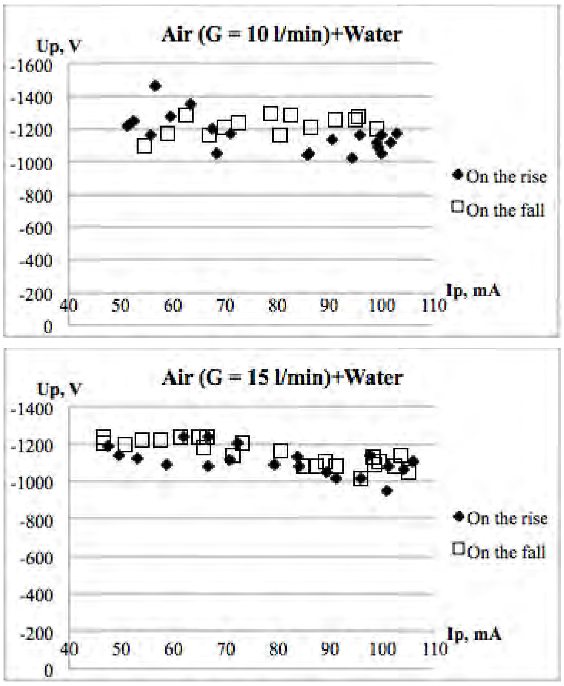

Fig. 9. Volt-ampere characteristics of the primary discharge for different plasma-forming gas flow rates determined from oscillograms

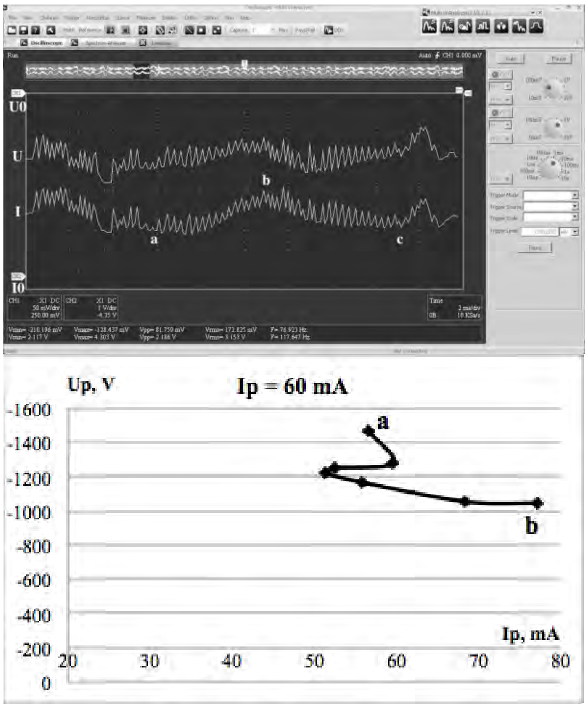

Fig. 10. Oscillograms of current and voltage at primary discharge current Ip=60 mA, G =10 l/min. CH1 voltage 50 mV/division (voltage divider 1:10.000), CH2 current 1 V/division (measuring resistor 50 Ω). The VAC is built on a time interval abc equal 11 ms

The characteristics do not change when the current changes within the studied range.

Figs. 10 and 11 shows the example of the oscillograms based on which the VAC curve was built and demonstrates, based on this oscillogram, how the current and voltage fluctuate during the discharge burning time at a fixed current.

voltage fluctuate during the burning time of the discharge within the sawtooth component.

Current fluctuations amount to ± 15 mA.

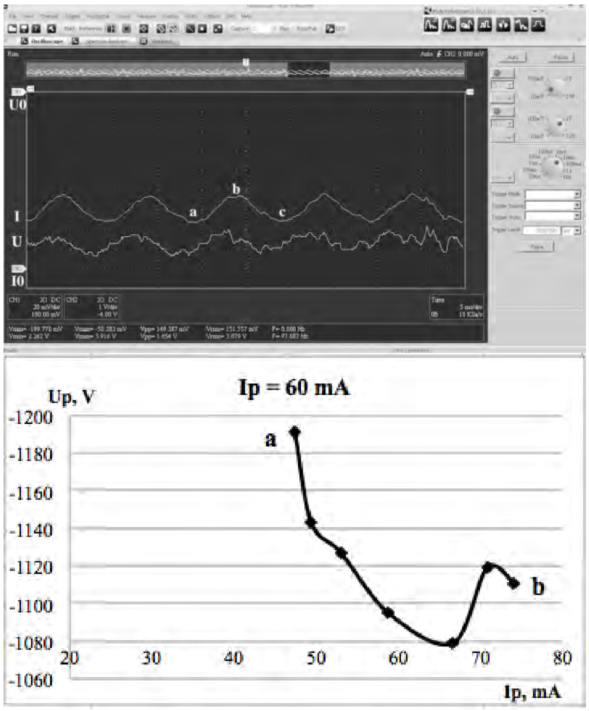

Fig. 11. Oscillograms of current and voltage at primary discharge current Ip=60 mA, G =15 l/min. CH1 voltage 20 mV/division (voltage divider 1:10.000), CH2 current 1 V/division (measuring resistor 50 Ω). The VAC VAC is built on a time interval abc equal 10 μs

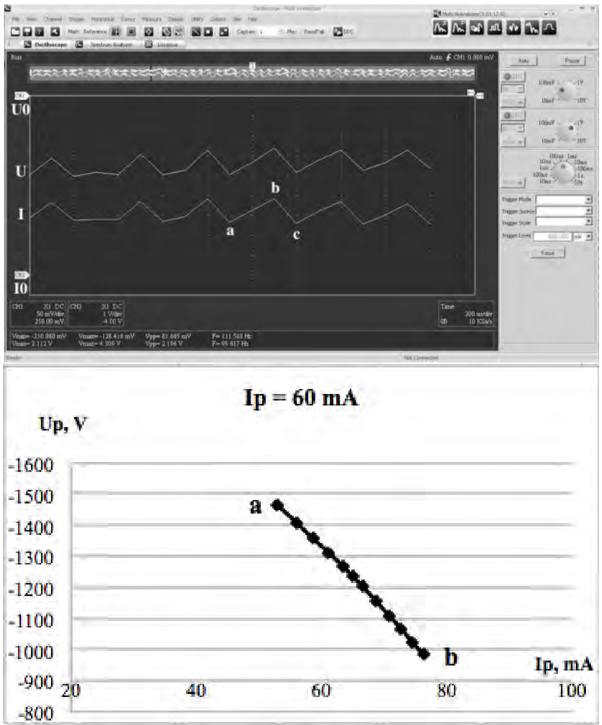

Fig. 12. Oscillograms of current and voltage at primary discharge current Ip=60 mA, G =10 l/min. CH1 voltage 50 mV/division (voltage divider 1:10.000), CH2 current 1 V/division (measuring resistor 50 Ω). The VAC is built on a time interval abc 300 μs

As we can see, with increased gas flow, the sawtooth component disappears.

Fig. 12 shows an example of oscillograms for an airflow of 10 l/min, discharge current Ip = 60 mA, and shows, based on these oscillograms, how the current and voltage fluctuate during the burning time of the discharge within the sawtooth component.

2.2. RESULTS OF OPTICAL DIAGNOSTICS OF PLASMA

The emission spectrum of the rotating gliding discharge plasma is presented in Fig. 13.

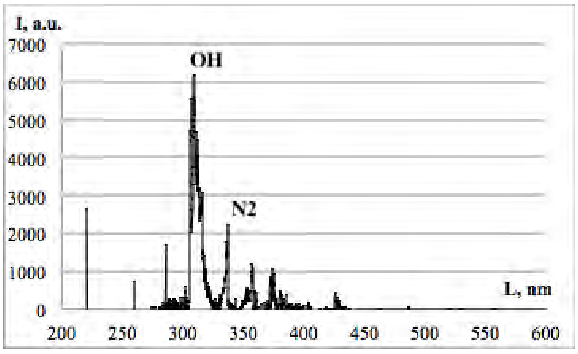

Fig. 13. The emission spectrum of the rotating gliding discharge plasma

Fig. 14 shows population temperatures obtained using dependencies $T(I_i/I_k)$ for different primary discharge currents. Air flows of 10 and 15 l/min were fed to the system. The discharge was immersed in the distillate with a volume of 100 ml.

The temperature of electron levels population (T*e) is greater than the temperature of vibrational and rotational levels population (Tv, Tr). This indicates that the plasma of the rotating gliding discharge is non-isothermal.

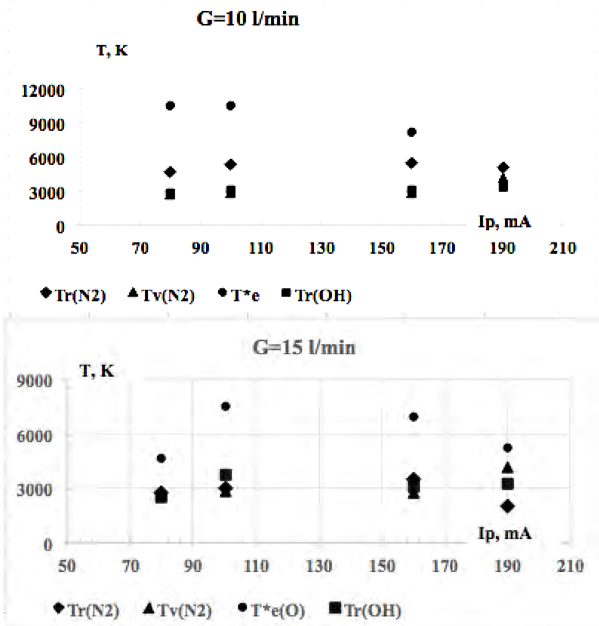

Fig. 14. Dependence of the temperatures of the population of O I electron levels, N_2 vibrational levels and N_2 and OH rotational levels on the primary discharge current for different air flows

The temperatures of the population of the vibrational and rotational levels of the N_2 molecule and the rotational levels of the OH molecule at an airflow of 15 l/min are the same within the margin of error (~ 3.000 K).

In the mode of operation with a secondary discharge, the current of the primary discharge was fixed at a certain value (100 and 160 mA), and the current of the secondary discharge was changed in the range from 40 to 100 mA (Fig. 15). The volume of distillate in the system was the same –100 ml. Air flow rates amounted to 10 and 15 l/min.

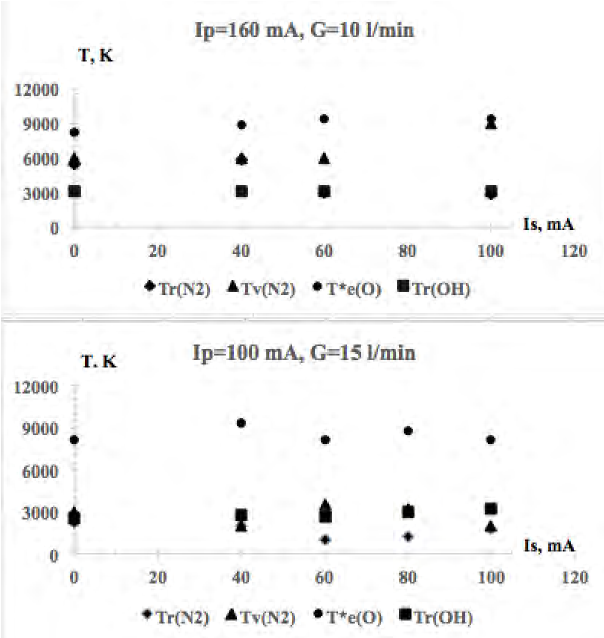

Fig. 15. Dependence of the temperatures of the population of O I electron levels, N_2 vibrational levels and N_2 and OH rotational levels on the secondary discharge current at fixed primary discharge currents for different air flows

The temperature of O I electron levels population T^*_e ≈ 8.000 K of the secondary discharge plasma at the primary discharge current Ip = 160 mA and air flow 10 l/min. The vibrational levels population temperature is higher than the N_2 rotational levels population temperature. The OH rotational levels population temperature is equal to ≈ 3.000 K and is close to $T_r(N_2)$. That is, the secondary discharge plasma is also non-isothermal.

At a fixed primary discharge current Ip = 100 mA and an air flow of 15 l/min. The temperatures of the population of N_2 vibrational and rotational levels and the temperature of the population of OH rotational levels are the same within the margin of error ~ 3000 K. However, there is a significant gap in the population temperature of electron levels. This indicates that in this mode of operation, the secondary discharge plasma is also non-isothermal.

Fig. 16 shows results for the system operation mode when N_2 was used as the plasma-forming gas. The results are presented for two operating modes of the system: the mode when only the primary Ip discharge burned (the current varied from 40 to 200 mA); the mode when the primary Ip and secondary Is discharges burned (the current of the primary discharge Ip was fixed at 100 mA, and the current of the secondary discharge Is varied from 20 to 100 mA). The flow of N_2 was 10 l/min. 100 ml of distillate was poured into the system.

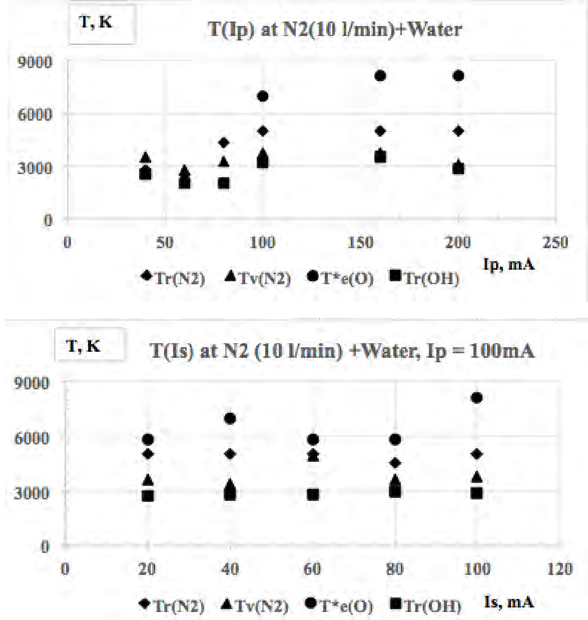

Fig. 16. Dependence of the temperatures of the population of O I electron levels, N_2 vibrational levels and N_2 and OH rotational levels on discharge currents

In the same way as for the operation mode with air when only the primary discharge was burning, the population temperatures obtained for N_2 and OH were the same within the margin of error ≈ 3.000 K. The O I electron levels population temperatures ≈ 8.000 K. For the mode when both discharges were burning, the population temperatures of N_2 vibrational levels and OH rotational levels were the same within the margin of error ≈ 3.000 K. The population temperatures of N_2 rotational levels are higher than Tv and amount to ≈ 5.000 K. The electron levels population temperature amounts to ≈ 6.000 K. It can be stated that the plasma of the rotating gliding discharge and of the secondary discharge is non-isothermal.

2.3. SOLUTIONS TREATMENT RESULTS

As a result of the treatment of the obtained solutions with the immersed discharge system, the following conclusions can be drawn based on visual observations:

1. As a result of plasma chemical synthesis in the nitrogen, water and ammonium molybdate system, the formation of molybdenum blue was recorded. This indicates the formation of a recovering agent in the reaction mixture (atomic hydrogen) and the recovery of Molybdenum (VI) ions to oxidation states (IV-V).

2. The nickel chloride solution changed its color from light green to brown with the formation of a precipitate.

3. The cobalt chloride solution color remained original without the formation of a precipitate, that is, no recovery or hydrolysis reactions were recorded.

4. Alcoholic solutions of organic compounds did not change their color as a result of plasma chemical synthesis, their composition was studied using nuclear magnetic resonance (NMR).

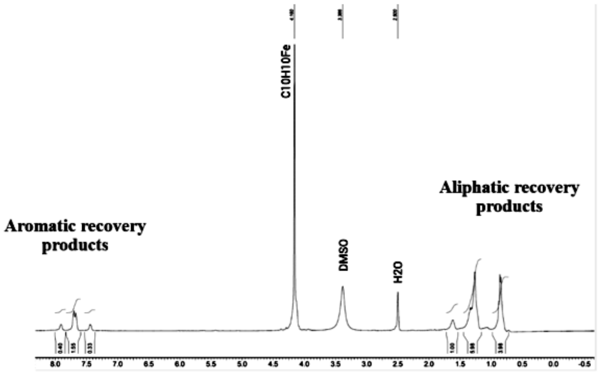

Fig. 17. NMR spectrum of ferrocene and its recovery products

For ferrocene, the destruction and recovery of cyclopentadienyl ligands to aliphatic and aromatic hydrocarbons was recorded, as evidenced by the appearance of signals in the ^{1}H NMR spectrum at 0.8…1.3 and 8 ppm (Fig. 17). The chemical composition of benzotriazole did not change, and no recovery products were recorded.

CONCLUSIONS

The paper demonstrated the following:

1. The plasma of a rotating gliding discharge immersed in a liquid and a secondary discharge supported by a rotating gliding discharge is non-isothermal.
2. Population temperatures of vibrational and rotational levels for a nitrogen molecule N_2 are the same within the margin of error ≈ 4.500 K.
3. The electron levels population temperature amount to ≈ 8.000 K.
4. The population temperature of the OH rotational levels and N_2 rotational levels are the same within the measurement error.
5. The ability to perform the redox of inorganic substances with a change in the metal's valency has been demonstrated.
6. One-stage conversion of cyclopentadienyl ligands into aromatic hydrocarbons is performed, which is only possible in chemistry through a multi-step process.

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РЕАКЦІЇ ДИСПРОПОРЦІОНУВАННЯ ФЕРРОЦЕНУ У ПЛАЗМОВО-РІДИННІЙ СИСТЕМІ З ОБЕРТОВИМ КОВЗНИМ РОЗРЯДОМ

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Досліджено плазмово-рідинну систему з активацією дистиляту H_2O та 0,1 М розчину ферроцену в органічних розчинниках (етанолі, ацетонітрилі) плазмою обертового ковзного розряду. Дослідження проведено з використанням різних плазмоутворюючих газів (повітря, Ar, N_2, CO_2). Визначення параметрів плазми проведено методами емісійної спектроскопії плазми. Показано, що плазма як обертового ковзного розряду, так і плазма вторинного розряду, підтримуваного ковзним розрядом, є неізотермічною. Дослідження фізико-хімічних властивостей продуктів синтезу проведено методами адсорбційного, люмінісцентного аналізу, поляриметрії, хромато-масспектрометрії, ЯМР. Виявлено, що циклопентадієнові ліганди ферроцену диспропорціонують на насичені циклічні вуглеводні (циклопентан та пентан). Також у результаті плазмохімічного синтезу утворюються ароматичні сполуки (бензол та його похідні).